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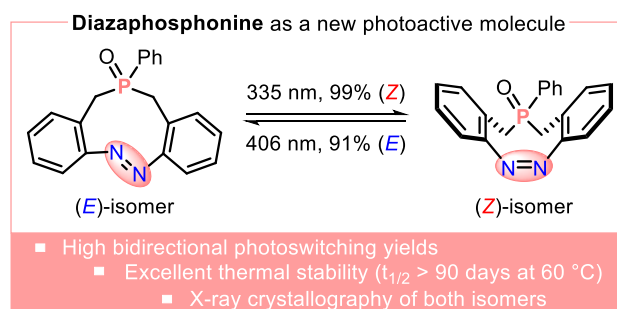
Synthesis and Characterisation of a [1,2,6]Diazaphosphonine Oxide: an Example of Photoswitchable, Phosphorus-Containing Cyclic Azobenzene

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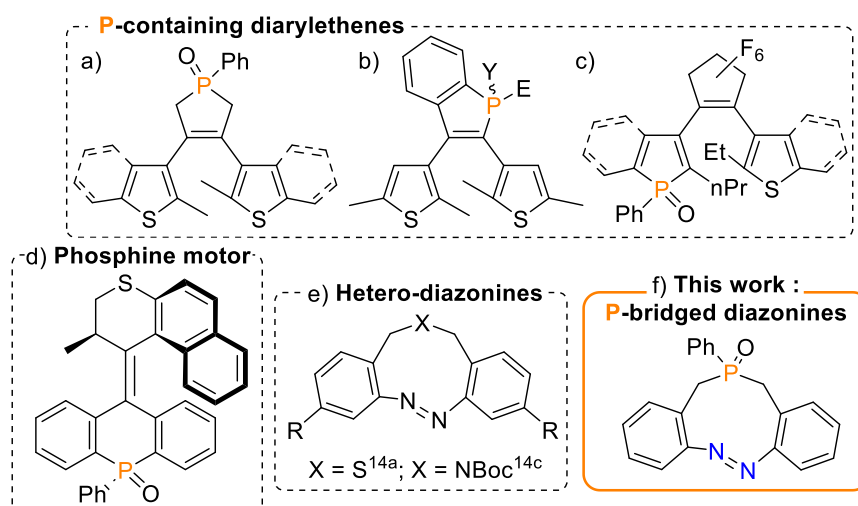
ABSTRACT: We report herein the synthesis and characterisation of a phosphorus-containing cyclic azobenzene, as a new photoswitchable scaffold. This backbone reveals high bidirectional photoswitching yields and high thermal stability of both isomers, with $t_{1/2} > 90$ days at 60 °C. Both *E*- and *Z*-isomers have been characterised by UV-vis spectroscopy and X-ray crystallography.

Molecular photoswitches allow high spatiotemporal control of a number of chemical and physicochemical properties and, consequently, the control of processes with relevance to different research areas, such as material sciences,¹ life sciences² or catalysis.³ Photoswitchable molecules are typically organic compounds with extended conjugated systems that make them light-responsive. Well-known classes include diarylethenes (DAE),⁴ Stiff-stilbenes⁵ and

azobenzenes,⁶ whose properties have been extensively and finely tuned by structural changes, including notably incorporation of heterocyclic units in their switchable frameworks.⁷ Among others, photoswitchable molecules featuring phosphorus heterocycles have received attention in recent years as advanced materials,^{8a} following the general emergence of phosphorus-based materials in the field of organic electronics.^{8b-c}

In 2008, Favaro and Moustrou have designed phospholene-fused dithienylethenes (DTE) as a new series of efficient photochromic molecules (Scheme 1a).⁹ In these compounds, the *P*-containing ring embeds the ethene unit of DTE. An analogous design has been developed then extensively by Yam and coworkers who investigated notably benzo[*b*]phosphole and thieno[2,2-*b*]phosphole fused DTEs and related structures, that demonstrated unprecedented photophysical properties, due to the extended π -system and electronic properties of the phosphole units (Scheme 1b).^{10a-e} As an alternative, Ragona and coworkers have reported on dihydro-1,3,2-diazaphosphole fused DTE derivatives that were used to incorporate switchable units into polymers.^{10g}

Scheme 1. Photoswitch compounds featuring *P*-heterocyclic units and proposed target.



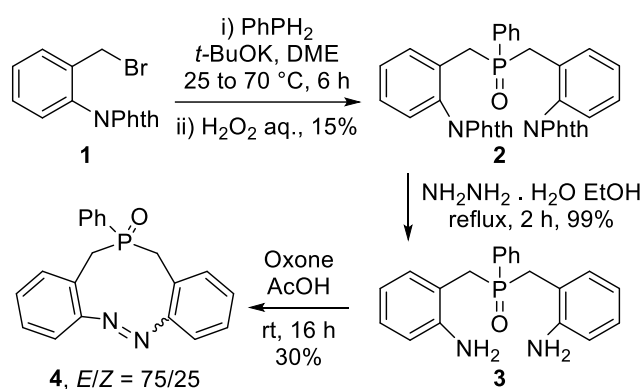
A different class of compounds has been introduced then by Morimoto and coworkers who designed hybrid DAEs featuring a (benzo)phosphole ring as one of the photoactive aryl units

(Scheme 1c).¹¹ More recently, Feringa and coworkers reported three new axially chiral molecular motors featuring a dihydroacridophosphine motif (Scheme 1d).¹²

This brief literature survey shows that not so much molecules featuring phosphorus heterocycles in their photoswitchable core are known to date, and none of them have been built on azobenzenes.¹³ In particular, medium-sized cyclic azobenzenes, such as hetero-diazocines and diazonines (Scheme 1e^{14a,c}), lacks of phosphorus analogues. This may be especially surprising as (hetero)cyclic azobenzenes, with eight¹⁵ and nine-membered rings¹⁴ are known to have complementary and possibly improved photophysical properties, compared to acyclic species. Moreover, the nature of the heteroelement is known to modulate their intrinsic properties.^{15b,c} Therefore, with the aim of filling this particular gap, we have targeted the synthesis and characterisation of a medium-sized cyclic azobenzene with a phosphorus unit embedded in the cyclic moiety itself,¹⁶ namely the 12-phenyl-11,13-dihydrodibenzo[*c,h*][1,2,6]diazaphos-phonine 12-oxide shown in Scheme 1f.

The targeted diazaphosphonine oxide **4** was synthesized in three steps from 2-(2-(bromomethyl)phenyl)isoindoline-1,3-dione **1**¹⁷ and phenylphosphine (Scheme 2).

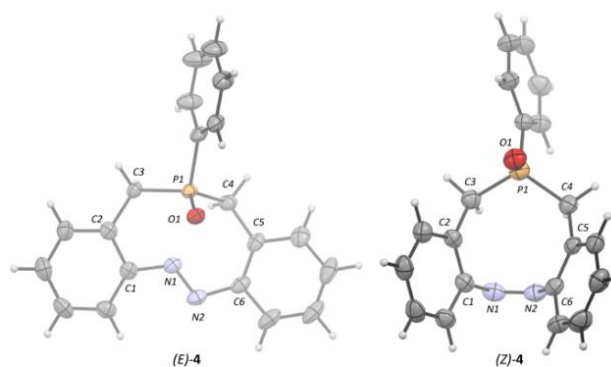
Scheme 2. Synthesis of diazaphosphonine **4** (NPhth = phthalimidate).



The first step is the double alkylation of phenylphosphine with benzyl bromide **1**, followed by *in situ* oxidation of the trivalent phosphine with hydrogen peroxide to provide phosphine oxide **2**. The phthalimide protecting groups are then removed with hydrazine, to give the bis-aniline **3** in 99% yield. The key step, namely the oxidative cyclization reaction, was carried out with

oxone in acetic acid at room temperature.^{14b,c} The desired dihydrodibenzodiaza-phosphonine oxide **4** was isolated in 30% yield, as a 75/25 mixture of *E* and *Z* isomers. The new compounds (*E*)-**4** and (*Z*)-**4** have been characterised by NMR, UV-vis spectroscopy absorption and X-ray crystallography. ORTEP (Oak Ridge Thermal Ellipsoid Plot) views for (*E*)-**4** and (*Z*)-**4** are displayed in Figure 1, together with selected bond distances and angles.

In the (*E*)-**4** isomer, the N=N bond distance measures 1.246 Å and the C1–N1–N2–C6 dihedral angle measures 176.7°. Especially, the distortion from planarity is significantly reduced, compared to the (*E*)-triazonine analogue **5** (Figure 2), in which the dihedral angle C1–N1–N2–C6 measures 163°.^{14c} Such a release of the ring strain in the (*E*)-diazaphosphonine can be assigned to the increased length of the P–C bonds, compared to N–C bonds: the intracyclic P–C bonds in (*E*)-**4** measure indeed 1.83 Å, while N–C bonds in the (*E*)-triazonine **5** measure an average of 1.47 Å.



Bond lengths (Å)		Bond and torsion angles (°)	
<i>(E)</i> - 4 / <i>(Z)</i> - 4 isomers		<i>(E)</i> - 4 / <i>(Z)</i> - 4 isomers	
N1–N2	1.246(5) / 1.249(2)	N2–N1–C1	114.8(3) / 119.9(2)
N1–C1	1.408(5) / 1.446(2)	N1–N2–C6	115.2(3) / 119.7(2)
N2–C6	1.423(5) / 1.450(2)	N1–C1–C2	118.8(3) / 119.9(2)
C1–C2	1.410(3) / 1.386(2)	N2–C6–C5	118.0(3) / 120.2(2)
C6–C5	1.395(6) / 1.388(5)	C1–C2–C3	122.3(3) / 121.7(2)
C3–P1	1.830(4) / 1.809(4)	C6–C5–C4	122.9(4) / 121.1(2)
C4–P1	1.835(4) / 1.802(3)	C2–C3–P1	117.6(3) / 116.6(2)
C7–P1	1.820(3) / 1.792(3)	C5–C4–P1	117.4(3) / 114.1(2)
P1–O1	1.484(3) / 1.466(3)	C1–N1–N2–C6	176.7/3.2

Figure 1. ORTEP views of (*E*)-**4**, (*Z*)-**4** and selected bond lengths and angles.

It also appears that changing from a nitrogen to a phosphorus atom affects the whole solid-state geometry of the molecule. In (*E*)-**4** the phenylene rings are almost coplanar with the diazo unit (dihedral angles 6.6° and 10.6°), while they deviate strongly from the C-N=N-C plane in the corresponding triazonine (*E*)-**5** (dihedral angles 40.0° and 47.0°, Figure 2). In addition, ring strain is also intrinsically related to the percentage of p-character present in the involved atoms, as demonstrated by Ferao's work with smaller rings.¹⁸

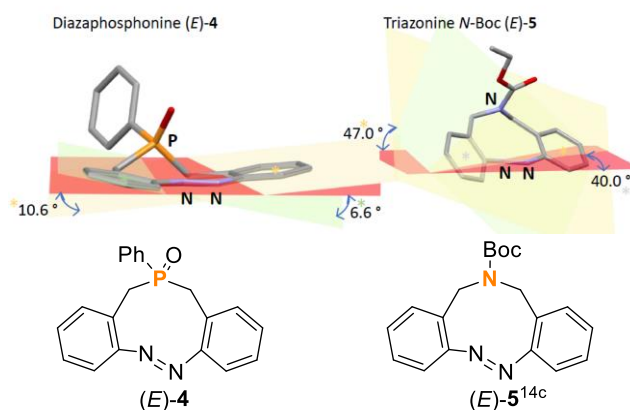


Figure 2. Comparison of the crystal structures of diazaphosphonine (*E*)-**4** and triazonine (*E*)-**5**.

The second isomer (*Z*)-**4** shows a N=N bond distance of 1.249 Å, which is in the expected range. The C1-N1-N2-C6 dihedral angle of 3.2° indicates an almost planar diazo moiety, suggesting a negligible ring strain. Overall, the U-shaped ring of (*Z*)-**4** strongly resembles that of the analogous triazonine (*Z*)-**5**. Thus, the nature of the heteroatom does not significantly alter the structural features of the *Z*-isomers, in contrast to the corresponding *E*-isomers.

The structural difference between the *E* and *Z*-forms of **4** can be illustrated also by comparing some of the non-bonding distances. For instance, the non-bonding distances between the carbon atoms *ortho* to the diazo group (*ortho* CH units) measure 5.10 and 3.40 Å for (*E*)-**4** and (*Z*)-**4** respectively, while the distances between the *meta* CH carbons are 7.81 and 4.96 Å respectively. Since the cyclic core scaffolds of (*E*) and (*Z*)-**4** are conformationally highly constrained, the X-ray crystal structures above should be roughly representative of the solution geometries of these

compounds and thus highlight the major structural changes that are expected from the *E/Z* photoswitch process.

Concerning the UV-vis absorption spectra (Figure 3a,b), the (*E*)-**4** isomer displays classic spectral features of *E*-azobenzene derivatives.⁶ The strong π - π^* band centered at 333 nm spans the 275-390 nm range, with a molar absorption coefficient (ϵ) of 18100 M⁻¹cm⁻¹. Thus, compared to the corresponding triazonine (*E*)-**5** that absorbs at 308 nm with $\epsilon = 6940$ M⁻¹cm⁻¹, the π - π^* band of (*E*)-**4** presents a significant bathochromic and hyperchromic shift (See Figure S6). Generally speaking, the ϵ value of (*E*)-**4** is two to three times higher than that of most cyclic azobenzenes. The very weak n- π^* band of (*E*)-**4** ($\epsilon = 250$ M⁻¹cm⁻¹) is centered at 440 nm in the visible region. In the UV-vis absorption spectrum of (*Z*)-**4**, the n- π^* band is blue shifted of about 40 nm, at 406 nm, with an increased absorption coefficient ($\epsilon = 325$ M⁻¹cm⁻¹).

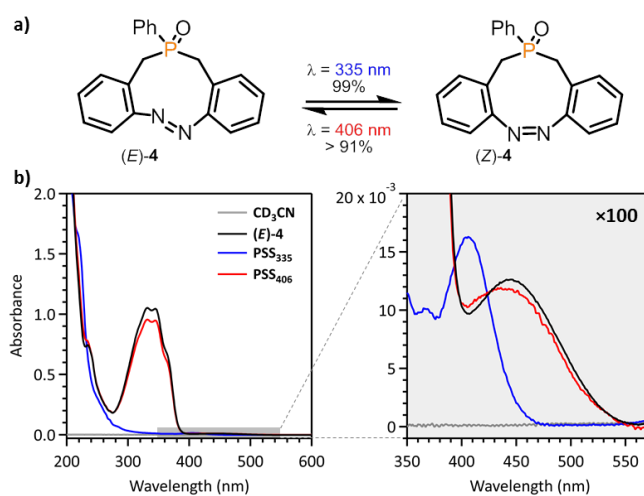


Figure 3. (a) (*E*)/(*Z*) photoisomerization of **4** under irradiation at 335 nm and 406 nm in CD₃CN via (b) UV-vis absorption ($C \approx 5.8 \times 10^{-5}$ mol L⁻¹).

The (*E*)-**4** to (*Z*)-**4** and the reverse *Z*→*E* photoisomerizations have been monitored in CD₃CN using UV-vis absorption and NMR spectroscopy. Under irradiation at 335 nm, the (*E*)-**4** isomer switches to the *Z*-form, reaching a photostationary state (PSS) at a *Z/E* ratio >99:1 (measured from UV absorptions, Figure 3b). Under visible light, at 438 nm, PSS reached 37% conversion.

The back switching to (*E*)-**4** was performed under irradiation at 406 nm to reach a PSS₄₀₆ with *E/Z* = 91:9, according to ¹H NMR analysis (See Supporting Information).

Overall, these experiments show that the diazophosphonine backbone undergoes a bi-directional switch with high conversion rates in both directions. Other PSS were also determined at higher wavelengths, showing that irradiation at 365 nm leads also to an excellent *E*→*Z* photoconversion yield (Figure 4a). Furthermore, diazophosphonine **4** demonstrated high fatigue resistance under alternating UV (335 nm) and visible (406 nm) irradiations in MeCN. Almost no photodegradation has been observed after 15 successive irradiation cycles.

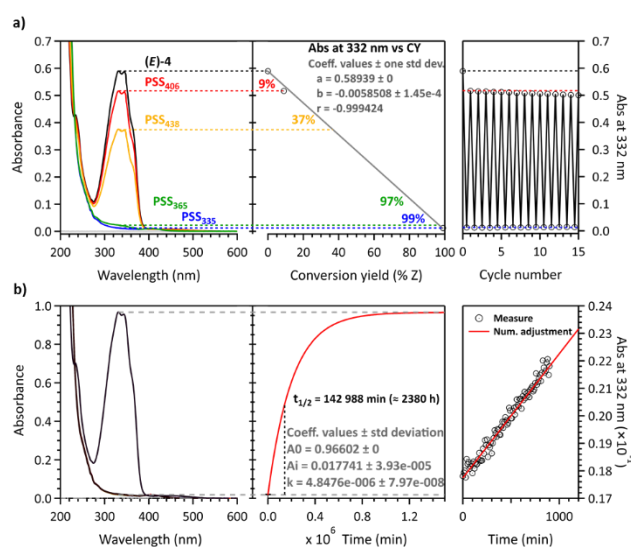


Figure 4. (a) PSS determination at different wavelengths and fatigue resistance after alternate irradiations at 335 nm (120 s; $P_{335} = 2.55 \text{ mW cm}^{-2}$) and 406 nm (780 s; $P_{406} = 8.26 \text{ mW cm}^{-2}$) in CH_3CN ($C \approx 3.3 \times 10^{-5} \text{ mol L}^{-1}$). CY: conversion yield. (b) Determination of $t_{1/2}$ of (*Z*)-**4** at 60 °C from the UV-vis absorption at 332 nm ($C \approx 5.3 \times 10^{-5} \text{ mol L}^{-1}$).

The thermal reversion of (*Z*)-**4** to (*E*)-**4** was monitored at 60 °C in acetonitrile, in the dark, by recording the UV-vis absorption spectra using a Peltier device. After 15 h, the variation in absorbance at 332 nm is negligible, and is estimated to be around $4 \cdot 10^{-3}$. A numerical fit estimated the half-life time of the (*Z*)-isomer at about 2380 h (99 days) at 60 °C (Figure 4b).

Thus, the half-life of the diazaphosphonine **Z-4** is significantly higher than that of the analogous triazonine **5** ($t_{1/2} = 19$ days at 60 °C in CDCl_3) and thiadiazonine **6** ($t_{1/2} = 0.5$ h at 25 °C, Figure 5). Geometry optimisations, performed by DFT calculations from X-ray data as a starting point for the atom coordinates, showed that the energy difference between *E*- and *Z*- isomers of **4** was 7.51 kcal mol⁻¹. It was calculated at 3.34 kcal mol⁻¹ for compound **5** (see Supporting Information).

Overall, the introduction of a phosphorus atom in the diazonine ring increases both the *Z/E* photoconversion rates and the lifetime of the *Z*-form, compared to the nitrogen and sulfur analogues, and also compared to other cyclic and acyclic azobenzene derivatives.^{6,14-15}

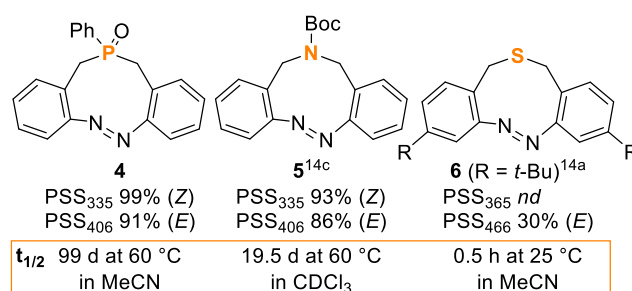


Figure 5. Comparison of the photostationary states, conversion yields and $t_{1/2}$ of the *Z*-forms of heterodiazonines **4-6**. *nd* = not determined.

To conclude, we have presented here the first synthesis of a nine-membered cyclic azobenzene embedding a phosphorus atom in the ring. It reveals excellent properties such as the thermal stability of both the (*E*) and (*Z*)-isomers, with negligible conversion of the *Z*- to the *E*-form at 60 °C. The bistability of the compound at r.t. allowed us to isolate both isomers and to obtain their crystallographic structures. Other interesting features of these molecules are the high photoconversion yields for both *E*→*Z* and the reverse *Z*→*E* isomerization processes and the excellent fatigue resistance after successive UV-vis irradiations. This scaffold therefore

represents a new photoswitchable core structure possibly adapted to different applications, from materials science to catalysis.

DATA AVAILABILITY STATEMENT

The data underlying this study are available in the published article and its Supporting Information.

SUPPORTING INFORMATION STATEMENT

Experimental details (including NMR spectra and photochemical and photophysical characterisations of *E-4* and *Z-4*) are given in the Supporting Information. CCDC Deposition Numbers 2171478 (for *E-4*) and 2171479 (for *Z-4*) contain the supplementary crystallographic data for this article. These data are provided free of charge by the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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