

Twisting Fate: Ring Torsions and Photochemistry in Aryl-X=Y-Aryl Systems (X,Y = P, C, N)

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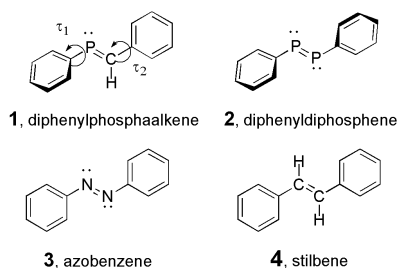
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Over the past 30 years or so, the design and synthesis of molecules has been transformed by chemists increasingly interested in imparting controllable functionality to their molecular architectures. One of the most widely exploited control processes is $E \rightarrow Z$ photoisomerization, particularly in azobenzenoid (Ar-N=N-Ar) and stilbenoid (ArCH=CHAr) molecules. Molecular switches, memory elements, capacitors, sensors, modulators of liquid crystal optical properties, organic light-emitting diodes (OLEDs), and other photon-driven materials have been explored with success.¹ The patent literature abounds with hundreds of photoisomerization-based ideas, from portable body warmers² to solar energy collectors and storage elements.³

As development of these systems continues, the exploration of the relatively untravelled regions of the periodic table in search of new molecules, materials and reactions continues. Phosphorus was long thought to eschew multiple bonds. In fact, this *double bond rule* once applied to all elements beyond the first row of the periodic table, where carbon, nitrogen and oxygen are so prolific in forming multiple bonds. In 1981, however, Yoshifuji and co-workers reported the first stable diphosphene (P=P) molecule.⁴ Since then, well over 100 compounds with multiple bonds involving atoms such as Si, Ge and As have been reported.

Multiple bonds among heavier main group elements tend to exhibit higher reactivity than their carbon and nitrogen cousins. However, with sufficiently bulky ligands, multiple bonds involving P, As, Si, Ge, and others can be successfully stabilized kinetically and studied. Knowledge of the synthesis, structures, coordination chemistry and reactivity of these compounds is at a relatively advanced stage, and has been reviewed recently.⁵⁻⁹ Less thoroughly investigated, but equally important for understanding and exploiting photocontrollable behaviour, is the photochemistry and photophysics of these systems.

Chart 1



Recently, we began a productive collaboration with a group that synthesizes diphosphenes (P=P) and phosphalkenes (C=P) for use in photochemically active materials. As a natural first step towards a thorough understanding of their photochemistry and photophysics, we applied both theoretical chemistry and ultrafast spectroscopy to study the ground and electronic excited states of some of these promising new molecules. Our previous studies have shown that the phenyl twist angle in aryl-substituted diphosphenes has a significant impact upon the ordering of the frontier orbitals and the oscillator strength of the major ultraviolet-visible (UV-vis) absorption transitions.¹⁰ We have now extended those studies to aryl-substituted phosphalkenes, and compare both the ground state isomerization (Fig. 1) and phenyl twist barriers (Fig. 2) to those of P=P, C=C, and N=N analogs. All of the model compounds studied here (Chart 1) either exist and undergo photoisomerization (stilbene¹¹, azobenzene¹²) or possess experimental analogs known to undergo photoisomerization.¹³⁻¹⁶ The results shed light on important differences in bonding among the main group elements, and help build a useful framework within which to interpret ongoing and future photochemical and photophysical research.

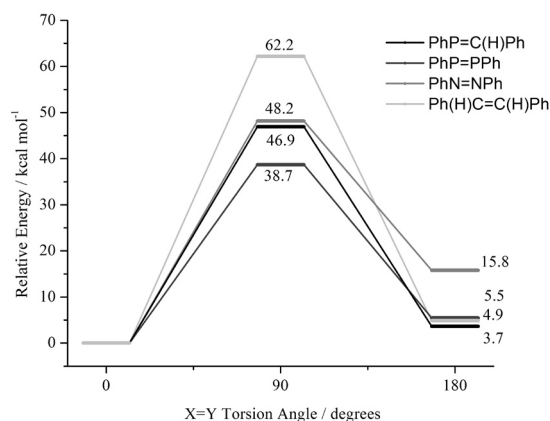


Fig. 1. $\Delta E(E-Z)$ and rotational barriers for torsions about the central X=Y double bond, where X,Y = C, N, P; calculations at the B3LYP/6-31+G** level.

Computational Methods

All computations were performed with the Gaussian 03 (rev.D.01) software package¹⁷ with density functional theory (DFT) using the B3LYP hybrid functional¹⁸ and 6-31+G** basis set.¹⁹ This level of theory was chosen as a reasonable balance between computational expense and accuracy. The discussion herein focuses upon ground state structures and energies, and vertical transitions to lower-lying excited states, and not chemical reactivity, *i.e.* no bond breaking or forming processes, and no

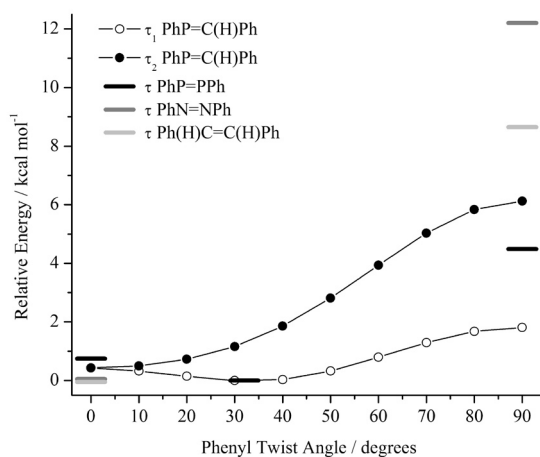


Fig. 2. Rotational barriers for torsions about the X-Ph single bond (X = C, N, P); calculations at the B3LYP/6-31+G** level with τ_1 referring to torsion about the P-Ph bond and τ_2 to torsion about the C-Ph bond.

intermolecular interactions. The B3LYP hybrid functional, by far the most widely used in recent times, performs well for the target outcomes in main-group chemical systems of similar sizes and complexity.²⁰

Many experimental diphosphenes and phosphalkenes attach phenyl-based bulky groups to the phosphorus (and carbon) atoms to kinetically stabilize the double bond. PhP=CHPh was thus chosen to include authentic molecular features such as conjugation and π -interactions, and to approximate steric interactions. Ground state structures were calculated for PhP=CHPh with appropriate constraints on the phenyl ring twisting coordinates, followed by time dependent DFT calculations (TDDFT) for the excitation energies, *i.e.* TDDFT-B3LYP/6-31+G**//B3LYP/6-31+G**. The potential energy surface was calculated at 10° intervals along the τ_1 (C=P-Ph) and τ_2 (P=CHPh) twist coordinates (see Fig. 1). The ground state (S_0) *E* (*trans*) to *Z* (*cis*) isomerization barrier was also calculated. The results are compared to findings from previous studies on PhP=PPh, PhCH=CHPh, and PhN=NPh at the same level of theory.

Aryl-X=Y-Aryl Bonding

Background

One area of critical interest is the nature of the heavier main-group multiple bond and its effect upon structures, properties, and reactivity.^{5,6,7,21,22} From the relative energies of the σ and π bonds in homonuclear double-bonded species (Table 1),^{5,24} first row atoms clearly behave differently from those in lower rows of the periodic table. While the π -bond is of comparable or greater strength than the σ -bond for C, N and O, heavier main group elements have relatively weak π bonds. While chemists tend to think of the first long row of the periodic table as the well-behaved one, it is actually the anomaly.²¹ Carbon is perhaps the epitome in this respect with nearly equal σ and π bond strengths (σ/π ratio = 1.14; the others vary from 1.41 for P to 1.73 for S) and this is the origin of the diversity of the stable compounds that it forms.

Table 1. Relative σ/π bond energies for homonuclear diatomics (kcal/mol)^a

C=C 80/70	N=N 38/94	O=O 35/83
Si=Si 46/28	P=P 48/34	S=S 64/37
Ge=Ge 39/26	As=As 42/29	Se=Se 50/30

^aData taken from reference 21.

The next closest σ/π ratio to carbon belongs to phosphorus. This is a manifestation of the increasingly apparent diagonal relationships in the periodic table. Phosphorus compounds often behave more like their carbon analogs than their directly vertical nitrogen neighbors.²⁵ Similarly, carbon resembles phosphorus more than silicon in many ways. For example, the electronegativities of carbon and phosphorus are comparable at 2.5 and 2.2, but quite different from those of Si (1.7) and N (3.1).

A classic analysis of bonding in heavier main group elements invokes relatively poor hybridization of orbitals to account for differences between first and later row compounds, including the greater propensity of first row elements to form multiple bonds, and for heavier elements to form hypervalent compounds.²¹ The commonly assumed fixed relationship between the degree of hybridization, *i.e.* s and p contributions to the molecular orbitals, and bond angles is not justified beyond $n = 2$.²² So why do heavier main group elements hybridize more poorly? Efficient hybridization occurs when the constituent atomic orbitals have similar energies and large spatial overlap. The relative energies of the atomic orbitals actually favour *more* hybridization for the heavier elements. The culprit is the very different valence s and p radial probability distributions for the first row compared to the others with s and p valence orbitals have approximately the same radial extent; the heavier elements have the valence p orbital extend significantly beyond its s orbital partner. Thus, the degree of hybridization decreases and the lone pair adopts more s character going down the periodic column.

Aryl-X=Y-Aryl

The geometries predicted by the level of DFT used by us are remarkably good. For example, the C=P bond length calculated (1.695 Å) compares favourably to that in the crystal structure of (*E*)-(4-Br-2,6-Mes₂C₆H₂)-P=CH(4-BrC₆H₄) (1.682 Å), as do the P-C and C-C bond lengths and bond angles in the C-C=P-C central unit.¹³ Similarly, the calculated P=P bond length of 2.058 Å is quite similar to the experimental values of 2.046 Å and 1.985 Å for bis(2,4,6-Bu₃C₆H₂)diphosphene^{4,24} and bis(2,6-Mes₂C₆H₃)diphosphene,²⁶ respectively; bond angles also are reproduced well.

The *E*-isomer is the lower energy structure for all four molecules studied (Fig. 1). (*Z*)-PhP=CHPh is destabilized the least, with $\Delta E = 3.7$ kcal/mol; (*E*)-PhN=NPh is destabilized the most relative to its (*E*)-isomer ($\Delta E = 15.8$ kcal/mol). The barriers to rotation about the double bond can provide an estimate to the π bond strength, though the

results here point to some weaknesses inherent in using DFT for such evaluations. Fig. 1 indicates that the weakest π bond is found in the P=P molecule. The strongest is predicted to be C=C by a significant margin in contrast to what is predicted in Table 1. Finally, the π bond in PhP=CHPh is predicted to be of similar strength to that of PhN=NPh. Thermal isomerization rates have been observed for a few diphosphenes ($Z \rightarrow E$: $\Delta G^\ddagger \sim 20$ kcal/mol at 0 °C,¹⁶ $\Delta H^\ddagger = 29.5 \pm 1.4$ kcal/mol, and $\Delta S^\ddagger = 38 \pm 6$ cal/mol/K for a similar diphosphene¹⁴). The relatively large activation entropy may be due to steric crowding that is relieved by isomerization. Niecke *et al.*²⁷ have synthesized a diphosphene that equilibrates at 25 °C to a 6:11 mixture of *Z*- and *E*-forms, with thermal isomerization rates for both processes of $\sim 10^{-7}$ /s. The barrier height calculated here for the diphosphene is qualitatively consistent with these experimental measurements, though the experimental systems have much bulkier ligands.

Unfortunately, the order of the barrier heights for isomerization calculated by B3LYP is not consistent with the π bond strengths presented in Table 1. Most likely this is due to well-known difficulties in calculating the transition states of these molecules with single-reference methods; the transition states possess considerable biradical character.²⁸ CASPT2//CASSCF calculations are underway in our lab to better address these issues, and to examine the features of the ground state potential surface with greater fidelity. Of additional interest to the ground state rotational barrier is the thermal inversion coordinate and energetics. We are also using complete active space calculations to evaluate the excited states along these reaction coordinates.

The π orbitals of the phenyl ring substituents have the capability of interacting with the central double bond, to varying extents, in these compounds. The barrier height to twisting the phenyl ring gives an indication, albeit qualitatively, of the extent of π delocalization across the molecule (Fig. 2). The potential energy surface along the $>C=PPh$ torsion (τ_1) and $-P=CHPh$ torsion (τ_2) angles is shown in detail. Endpoint values of the other species discussed in this study are provided for ease of comparison.¹⁰

The ground state *E*-isomers of both PhN=NPh and PhCH=CHPh have planar minimum energy configurations of C_{2h} symmetry. In contrast, the Aryl-X=Y=Aryl molecules containing phosphorus are not planar. The phenyl ring attached to the P atom is twisted between 30° and 35° for both PhP=PPh and PhP=CHPh. In the latter

species, there is a slight phenyl twist (6°) about the C-Ph bond as well.

The lowest energy structures of these molecules reflect an intramolecular balance between the conjugation of the π system across the molecule that drives towards molecular planarity, and steric repulsions that induce non-planar configurations. In this case, phenyl twisting relieves repulsions between the large third-shell phosphorus lone pairs and phenyl *ortho*-hydrogens. These steric repulsions are further exacerbated by the small (ligand)-P=X angle (103° in both molecules), that is a consequence of the less effective sp^2 hybridization in heavier main group systems, as discussed above. The equivalent angles in PhCH=CHPh and PhN=NPh are much closer to 120°, as is the (ligand)-C=P angle in the phosphalkene studied here (127°). The energies at $\tau = 90^\circ$, where the phenyl ring is orthogonal to the central X=Y bond, indicate that the conjugation across the molecule is reduced for the phosphorus-containing molecules as well. In experimentally characterized diphosphenes and phosphalkenes, the use of bulky groups to protect the reactive double bond leads to a wide range of phenyl twist angles, most of which are greater than 45°. Our calculations confirm the suggestion that phenyl twisting provides an energetically thrifty path along which the molecule can relieve steric stresses. Furthermore, the small barriers indicate that at room temperature, the P-phenyl substructure samples a wide range of twist angles in solution.

Frontier Orbitals, UV-vis Transitions, and the Phenyl Twist

Previous studies in our group have found that the photochemically important order and energetic splitting between the two occupied frontier orbitals is exquisitely sensitive to twisting of the phenyl substituent rings relative to the C-P=P-C plane of a diphosphene.¹⁰ The transition energies and intensities of the first and second singlet states (S_1 and S_2) also depend upon the phenyl twist angle in diphosphenes and the possibility of analogous behaviour in the PhP=CHPh system demanded examination.

The situation in PhP=CHPh is a bit more complicated as more orbitals become involved and the degrees of freedom (τ_1 and τ_2) for the two phenyl ring twists are no longer identical. In the fully planar PhP=CHPh, the HOMO is a π -orbital, with bonding character across the P=C and an antibonding relationship between the P=C and the phenyl rings (Fig. 3). The next two orbitals are e_{1g} π orbitals

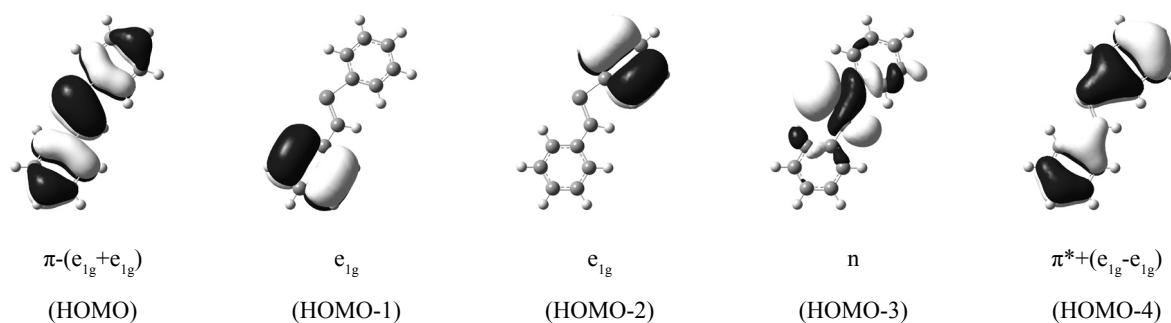


Fig. 3. The molecular orbitals most important for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions; calculations at the B3LYP/6-31+G** level.

localized on the phenyl rings; they are largely insensitive to the distortions cause by the phenyl twists. The n-orbital associated with the P-atom is HOMO-3. The last orbital of interest here is the HOMO-4, a π^{*+} orbital that has antibonding character at the P=C double bond, and bonding interactions with the phenyl rings.

As the phenyl ring attached to the P-atom is twisted, the π^- and π^{*+} orbitals are significantly stabilized whilst the n orbital is destabilized. At planarity (0° twist), the n and π^{*+} orbitals are within 0.2 eV of one another (Fig. 4). However, when orthogonal (90° twist), they have moved to *ca.* 1 eV difference in energy, with the π^{*+} being the energetically much more stable orbital. Furthermore, the π^- (HOMO) and n orbitals have moved considerably closer in energy to one another, though π^- is still the HOMO by about 0.8 eV. The π^- orbital remains the HOMO throughout the full range of τ_1 distortion from 0° to 90° . The P=CHPh moiety was held planar throughout this rotation for all calculations.

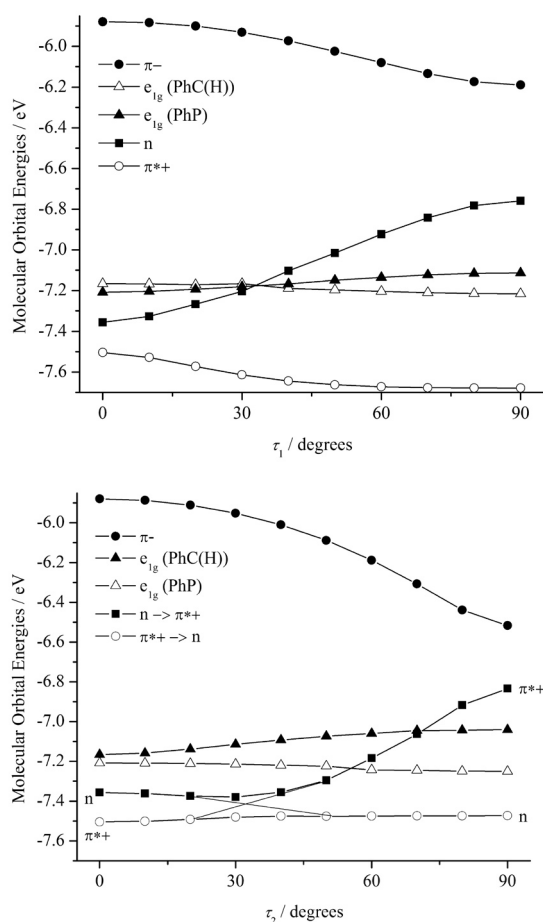


Fig. 4. Molecular orbital energies vs τ_1 and τ_2 ; calculations at the B3LYP/6-31+G** level.

The TDDFT-B3LYP/6-31+G**//B3LYP/6-31+G** calculations illustrate the impact of twisting the phenyl groups upon the two lowest energy electronic excitations (Fig. 5). For the planar molecule, the S_1 state is assigned to a $\pi-\pi^*$ transition (3.42 eV; 362.5 nm; $f = 0.611$), and the S_2 to the $n-\pi^*$ (4.042 eV; 306.7 nm; $f = 0.037$).¹³ Under the point group symmetry of the molecule, the $n-\pi^*$ is formally forbidden. However, it gains intensity by mixing with the nearby $\pi-\pi^*$ orbital. The experimental electronic

absorption spectrum for a phosphalkene with aryl groups at the C and P positions shows a broad peak at about 350 nm, in excellent agreement with the calculations.

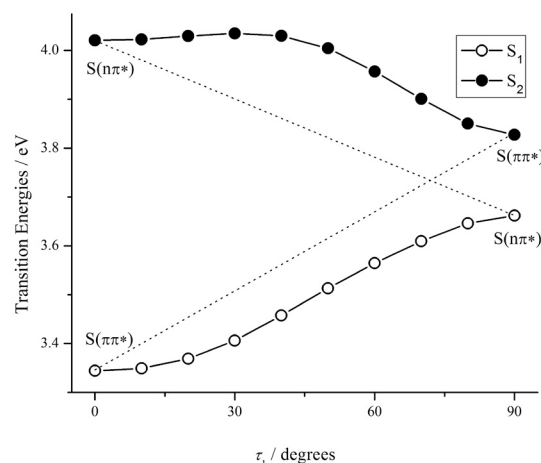


Fig. 5. Excited state (S_1 and S_2) energies vs τ_1 and τ_2 ; calculations at the TDDFT/6-31+G**//DFT/6-31+G** level.

Twisting the phenyl ring attached to the P atom leads to enhanced interaction between the two transitions, and eventually a swapping of the order of the states at $\tau_1 \sim 70^\circ$. In highly distorted systems, then, $n-\pi^*$ is expected to become the lower energy state but this may be difficult to see experimentally as it is expected to have the weaker intensity. Twisting the =CHPh phenyl ring at the other end of the molecule (τ_2) while holding the PhP=C architecture planar leads to somewhat different behavior. The most significant dissimilarity is a strong mixing between the n and π^{*+} orbitals that begins at around $\tau_2 = 20^\circ$. By $\tau_2 = 90^\circ$, the orbitals have nearly exchanged places. The HOMO-1 orbital is now mostly a π^{*+} orbital with strong polarization to the phosphorus lone pair, while HOMO-4 is dominated by phosphorus n contributions that are strongly polarized towards the phenyl ring. When the phenyl and central C=P units are orthogonal, the π^- (HOMO) and π^{*+} (HOMO-1) orbitals are within a few tenths of an eV of one another.

In addition to the mixing that occurs during phenyl rotation at the carbon, Fig. 4 also shows that HOMO stabilization is more dramatic for distortion along τ_2 than for displacement along τ_1 . That is, twisting the phenyl ring attached to the carbon has a larger impact upon π -bonding between the C and P than does twisting the phenyl ring attached to the phosphorus. This effect is probably due to the uneven contributions of carbon and phosphorus to the π -bonding interaction. The impact on the UV-vis absorption spectrum of twisting along τ_2 is significantly more complicated than that observed for the phenyl bound to the phosphorus (not shown), and is not yet fully understood. The S_2 ($n\pi^*$) state appears to have an avoided crossing with S_3 whilst the S_3 state ($e_{1g}\pi^*$) is in the $0^\circ < \tau_2 < 50^\circ$ region before it crosses the S_2 ($n\pi^*$) state ($\tau_2 \sim 75^\circ$) to become the HOMO when the phenyl ring is fully orthogonal. The S_1 and S_2 transitions mix, and eventually exchange their order so that at $\tau_2 = 90^\circ$ the S_1 state is $n\pi^*$ in nature. At about the same phenyl twist angle, the S_1 ($\pi\pi^*$) transition shifts to shorter wavelengths and eventually crosses the state just above it. Up until now this

complex behaviour has not been thoroughly interpreted, and studies are underway to gain further insight.

One important and unique feature of diphosphene systems is that the S_1 state does not primarily reflect an excitation from HOMO to LUMO.¹⁰ In the phosphalkene model studied here, this effect is not observed, save for the larger phenyl twist angles. In the diphosphenes, the effect is due largely to stabilization of S_1 through participation by transitions from the lower energy phenyl ring π orbitals to the π^* LUMO. As one might expect, this interaction is quite sensitive to the twist angle of the phenyl ring. In addition, the changes in the UV-vis absorption spectrum caused by phenyl twisting and predicted by the DFT and TDDFT computations of diphosphenes are mirrored in experimental observations across a wide variety of aryl-substituted diphosphene molecules.

Speculations Concerning Phenyl Twists and Photochemical Fates

It is well known that the frontier orbitals play a significant role in determining the chemical and physical fate of photoexcited molecules.²⁹ Thus, the potential impact of the phenyl twist upon diphosphene and phosphalkene photochemistry is significant. These molecules exhibit a rich diversity of photoprocesses. Diphosphenes have been shown to undergo many photoinduced reactions, including dimerization, metathesis, intramolecular ring formation, and cleavage.^{8,13-16,27-30} Of particular interest is the photoactivated *E*-to-*Z* isomerization reaction that has attracted so much attention for stilbenes and azobenzenes. Clearly, photoinduced isomerization occurs in some diphosphenes, and the *Z*-isomer of Mes*P=PMes* has been trapped by irradiation of the *E*-isomer under low temperature conditions.^{14,15} However, it is not clear whether all diphosphenes photoisomerize, how the isomerization occurs, or its role in subsequent photochemistry.¹⁴ Phosphalkenes also exhibit diverse photochemical behaviour, most notably in undergoing photoisomerization.¹³

The most natural approach to understanding these exciting new systems would be to build upon the extensive body of literature exploring stilbene and azobenzene photoisomerization. However, what these previous studies mean for diphosphene and phosphalkene photochemistry is unclear. The cognate electronic configurations of nitrogen and phosphorus suggest that photoisomerization in diphosphene is likely to mirror that of azobenzene. However, the diagonal relationships in the periodic table engender many surprising similarities between the properties of carbon and phosphorus compounds.²⁵ There is evidence of this in the present study as the barrier to torsion about the central double bond follows the nice trend of PhCH=CHPh > PhP=CHPh > PhP=PPh. Similarly, in diphosphenes the thermal isomerization barrier for inversion is significantly higher than that for rotation,^{10,28} while just the opposite is true for azobenzenes.

The relatively poor hybridization in heavier main group compounds, and the differences in relative π and σ bond strengths discussed above, offer uncertainty in predictions based upon similarities to compounds derived from the

first long row of the periodic table. While these issues have been considered extensively in reactivity and structure studies, their photochemical and photophysical consequences remain to be addressed. How does one think about photochemistry in molecules where *e.g.* a π bond can be weaker than a σ bond? What rules govern excited state geometries, barriers, and dynamics? What are typical excited state lifetimes, and what affects them? How do the photophysics and photochemistry of these systems relate to C=C- and N=N- counterparts? Do the diagonal relationships of the periodic table extend also to photodynamics? The studies reported here and elsewhere represent an important first step in addressing these critical issues.

Acknowledgment

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Dates of Note

Jan 17 marks the 50th anniversary of full energy release by the first synchrotron, which was installed at the Radiation Laboratory, Berkeley. On 19 Jan 1894, Prof **James Dewar** exhibited several properties of liquid air, and produced solid air, at the meeting of the Royal Institution. Jan 20 marks the 175th anniversary of the birth of **Adolf Frank** who invented the brown coloured beer bottle to preserve the ale.

Jan 22 marks the day 70 years ago when the uranium atom was split for the first time using the Columbia University cyclotron in New York; it marked the start of the Manhattan Project that gave us the atom bomb.

German-born **John Polanyi**, who shared the 1986 Nobel Prize for Chemistry (with Dudley R. Herschbach and Yuan T. Lee) for contributions to the *development of a new field of research in chemistry – reaction dynamics*, has his 80th birthday on Jan 23. Jan 25 is the 35th anniversary of **Barnard**'s pioneering transplant of the first human heart.

100 years ago on Jan 26 **Alexander King**, the Scottish chemist who pioneered in environmental awareness, was born. He warned of the dangers to the environment from extensive industrial development. Jan 29 marks the 75th anniversary of **Fritz Haber**'s death. He won the 1918 Nobel Prize for Chemistry (1918) for his ammonia synthesis. The 30th marks 50 years since the first use of a pacemaker.

On Feb 1 1959, Texas Instruments was issued a patent on the integrated circuit. **Dmitry Ivanovich Mendeleev** was born 175 years ago on Feb 8 while Feb 13 marks 175 years since the birth of **Heinrich Caro**, Technical Director of Badische Anilin & Soda Fabrik; he commercialized alizarin and indigo amongst others. **James Cook** died on Feb 14, 230 years ago.

The 150th anniversary of **Svante August Arrhenius**'s birth is on Feb 19; he received the 1903 Nobel Chemistry Prize. Sir **Ernest Marsden** was born on the same day in 1889.

Johannes Nicolaus Bronsted, the Danish chemist known for the acid-base concept, was born 130 years ago on Feb 22 and **Heinrich Hertz** the same day in 1857. It is also the day in 1828 that **Friederich Wöhler** informed Berzelius that he had synthesized urea. Feb 23 marks 55 years since the first mass inoculation with Salk polio vaccine was performed.

Feb 25 is the 10th anniversary of **Glen T. Seaborg**'s death; he was co-recipient of the 1951 Nobel Prize for Chemistry. The day also marks the birth of **H. H. Dow**, founder of Dow Chemical Company in 1866 and 180 years since the birth of **Levi Strauss**. Feb 27 marks 130 years since the discovery of saccharin, the artificial sweetener.

The first push-button telephone was put to test on 2 Mar 1959. The American biochemist **Elmer McCollum**, who originated the letter system of naming vitamins, was born on 3 Mar 1879 while **Gerhard Hertzberg** died 10 years ago this day.

Dmitry Mendeleev published his first version of the periodic table on Mar 6, 1899. **F. M. Crafts**, of Friedel-Crafts fame, was born on Mar 8, 1839; **Friedel** was born on Mar 12, 1832. Mar 14 marks 130 years since the birth of **Albert Einstein** and Mar 15 is the 5th anniversary of **John Pople**'s death; he devised the Gaussian suite of programmes.

Sir **Derek Barton** died 11 years ago on Mar 16. Mar 20, 75 years ago, saw the first test of a practical radar apparatus. On Mar 21, 1925, **Wolfgang Pauli** published his exclusion principle. 23 Mar 1989 saw the cold fusion announcement by electrochemists **Martin Fleischmann** and **Stan Pons**.

Mar 24 marks the 125th anniversary of the birth of **Peter Debye**, the Dutch physical chemist most noted for dipole moments and the unit of measurement named after him. **Johann Döbereiner** died on the same day in 1849; his observation of similarities among certain elements anticipated the development of the periodic system.

1 Apr deaths include **François-Marie Raoult** (1901) and Dame **Kathleen Lonsdale** (1971) and Apr 3 has to be noted as the 75th anniversary of the granting of a British patent to **Percy Shaw** for the *catseye road marker*. 6 Apr 1954 was the first day of sale of the TV dinner.

10 Apr marks the 55th anniversary of **Woodward** and **von Doering**'s synthesis of quinine. The 12th is the 125th birth date of **Otto Meyerhoff** who is known for his work on carbohydrate metabolism and the working muscle; he gained the 1922 Nobel Prize for medicine.

Apr 14 would have marked the 80th birthday of **Alan MacDiarmid**.