An aromatic–antiaromatic switch in P-heteroles. A small change in delocalisation makes a big reactivity difference†

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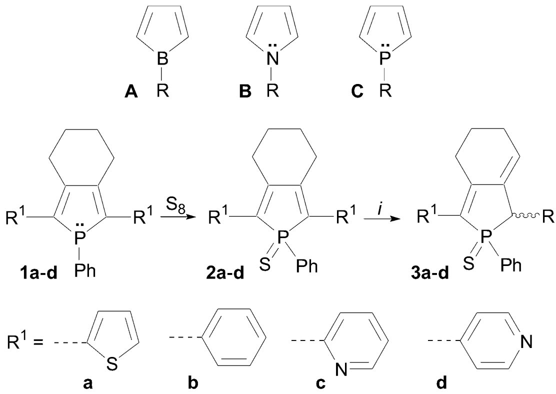
The low aromaticity of phosphole can be switched to low antiaromaticity by oxidizing the phosphorus atom. This subtle change in the mode of delocalisation alters substantially the chemical behaviour of these heteroles.

Aromaticity and antiaromaticity are fundamental and fruitful concepts to rationalise the stability and reactivity of annulenes.[1] In the case of heterocyclic derivatives, the nature of the heteroatom usually determines their aromatic or antiaromatic character.[1b,c] For example, borole **A** (Scheme 1) is strongly antiaromatic while pyrrole **B** exhibits a large aromatic stabilisation.[2] The aromaticity of phosphole **C** (Scheme 1) has long been debated. It is accepted now that it exhibits a small aromaticity arising from the interaction of the π-system not with the P-lone pair, but with the exocyclic σ(P–R) bond (hyperconjugation).[3] In this paper, we show that this unique situation offers the opportunity to switch from "slightly" aromatic to "slightly" antiaromatic species by chemical modification of the P-centre and that this switch has a considerable impact on the chemical properties of these heterocycles.



Scheme 1 *Conditions: i*, **3a**: refluxing xylene, Et_2NH, 1 day; **3b**: refluxing xylene, Et_2NH, 4 h; **3c, d**: 40 °C, THF, 2 days. Dotted lines show the connectivity of the R^1 substituents.

Phosphole-based derivatives **1a–c** (Scheme 1) have recently emerged as a novel class of π-conjugated systems.[4] One drawback of these assemblies is their relatively low thermal stability which is probably due to the isomerisation of the 1*H*-phosphole hearts into very reactive 2*H*-phospholes.[5] Interestingly, σ^4-thiophospholes **2a, b** (Scheme 1) exhibit higher thermal stability allowing these compounds to be used as multifunctional materials for OLEDs.[4c] This is likely due to the fact that the 1*H*-phosphole → 2*H*-phosphole isomerisation process is less favoured for σ^4-phospholes.[5b] Hence, chemical oxidation of the P-centre is a clue towards the optimization of the physical properties of these P-materials towards optoelectronic applications and we have tried to extend this methodology to other phosphole-based oligomers.

In contrast to what is observed in the thienyl and phenyl series, oxidation of the P-atom of 2-pyridyl- and 4-pyridyl-capped phospholes **1c, d** (Scheme 1) results in a decrease of their thermal stability. For example the decomposition temperature in the solid state, as estimated by thermogravimetric analysis, of σ^3-phosphole **1c** is 210 °C against 145 °C for its σ^4-derivative **2c**. The same trend is observed in solution. σ^3-Phospholes **1c, d** are stable in refluxing THF for weeks. In contrast, in THF at 40 °C, σ^4-thiophospholes **2c, d** quantitatively transform within two days into the corresponding phospholenes **3c, d** (Scheme 1). The structure of these novel derivatives was established by multinuclear NMR spectroscopic data (Table 1), high resolution mass spectrometry and elemental analysis. For example, the $^{13}C\{^1H\}$NMR spectra of the diastereoisomeric mixture of **3c** shows two doublets due to a PCH moiety (+55.4 ppm, J_{PC} = 51.3 Hz and +59.9 ppm, J_{PC} = 51.1 Hz) and only three remaining signals assignable to the CH_2 groups of the fused carbocycle. These NMR data are very similar to those of structurally related free or coordinated σ^3-phospholenes.[6] It is interesting to note that two diastereoisomers are also observed for **3d** at low conversion (^{31}P NMR: δ, +64.8 and +66.2). However, after completion of the reaction only one is obtained (Table 1) indicating a thermodynamically controlled process. These results prompted us to reinvestigate the thermal behaviour of 2-thienyl- and phenyl-capped σ^4-thiophospholes **2a, b** (Scheme 1) in detail. These compounds are stable in refluxing xylene (138 °C) for days. It is likely that the pyridine groups of **2c, d**, acting as a base, can catalyse the 1,3-shift leading to phospholenes **3c, d** *via* the formation of an allylic anion [Scheme 2, eqn (1)].[6,7a]

Table 1 Selected NMR Data (CD_2Cl_2) for phospholenes **3a–d**

	P–CH		
	$\delta\,^{31}P$, ppm	$\delta\,^1H$, ppm (J_{PH}, Hz)	$\delta\,^{13}C$, ppm (J_{PC}, Hz)
3a	+65.8/+64.6	5.41 (13.6)/4.90 (20.0)	54.6 (56.1)/54.3 (51.2)
3b	+66.9	4.66 (22.7)	59.6 (52.6)
3c	+66.4/+64.8	5.02 (16.5)/4.82 (11.8)	59.9 (51.1)/55.4 (51.3)
3d	+64.8	4.45 (10.8)	54.0 (50.3)

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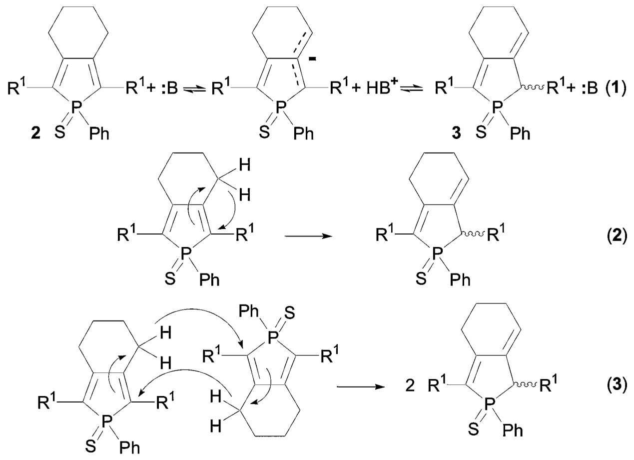
† Electronic supplementary information (ESI) available: Detailed description of the experimental procedure and total energies (in hartree) and optimized structures (in cartesian coordinates) of compounds **2a**, **c**; **3a**, **c**; **4a–e**, **5a–e**, **6a–e** and **7a–e** at the given levels of the theory. See DOI: 10.1039/b516836h



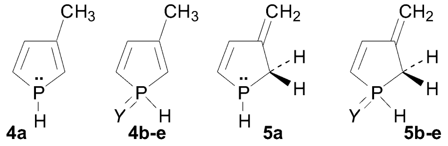
Scheme 2 Possible isomerisation mechanisms.

Hence, an excess of diethylamine was added to the refluxing xylene solution of **2a, b**. Indeed, under these harsh reaction conditions, the formation of the corresponding phospholenes **3a, b** is observed (Scheme 1, Table 1). The conversion of **2a** is not complete (yield *ca.* 50%) whereas **2b** is quantitatively transformed into **3b**.

Related σ^3-phosphole–σ^3-phospholene isomerisation is known to proceed in the coordination sphere of transition metals.[6,7b] However, this type of σ^4-phosphole–σ^4-phospholene transformation is unprecedented. In order to get more insight into this surprising isomerisation, quantum chemical calculations (B3LYP/6-31+G*)[8] were carried out for the 2-thienyl- and 2-pyridyl-capped series. Indeed, they revealed that σ^4-thiophosphole **2c** is less stable than σ^4-thiophospholene **3c** by 1.3 kcal mol^{-1}, while **2a** is somewhat (by 0.9 kcal mol^{-1}) more stable than **3a**. These results are in agreement with the experimental facts that the isomerisation is almost quantitative for **2c** and only partial for **2a** (conversion *ca.* 50%). Furthermore, these calculations show that one of the two diastereoisomers of **3c** (the one with a relative *trans* arrangement of the sulfur at P and of the pyridyl group) is more stable than the other one by 3.4 kcal mol^{-1}. This rationalizes that, in some cases (Table 1), only one diastereoisomer is obtained at high conversion.

To understand the origin of these effects and the isomerisation mechanism, the parent ring has been investigated. The σ^3-phosphole **4a** (Table 2) is more stable than its 2-phospholene isomer **5a** by *ca.* 5 kcal mol^{-1} (Table 2). In contrast, σ^4-thiophosphole **4b** (Y = S) is slightly less stable than its phospholene isomer **5b** (Table 2). Oxidation of the P-atom results in an inversion of the phosphole–phospholene thermodynamic stability. Note that (*i*) all σ^4-phospholes **4c–e** are also less stable than the corresponding phospholenes **5c–e** and (*ii*) the relative stability of **4b–e** decreases when the electronegativity of Y increases (series **b**/**c**, series **d**/**e**). The activation energy for the non-catalysed **4b–e** → **5b–e** transformation *via* a monomolecular [intramolecular 1,3-H shift, Scheme 2, eqn (2)] and a bimolecular [intermolecular H-transfer + isomerisation, Scheme 2, eqn (3)] processes is 85–89 kcal mol^{-1} and 47–55 kcal mol^{-1}, respectively, depending on the nature of Y (Table 2). These high energy barriers discard these two reaction paths since the isomerisation of **2c**, **d** into **3c**, **d** (Scheme 1) occurs at 40 °C, and there is no reason to believe that the presence of the R^1 substituents would lower these barriers considerably. It is thus probable that the isomerisation mechanism involves an intermediate allylic anion[6,7a] [Scheme 2, eqn (1)] as supported by the fact that this reaction is base-catalysed in the case of **2a**, **b** (Scheme 1). Hence, the conclusions of this theoretical study fit nicely with all the experimental observations.

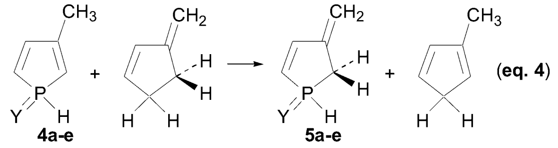
Table 2 Δ*E*: Relative energies of **4a–e** and **5a–e**; *E*(TS2) and *E*(TS3): relative energy of the transition states (**6a–e**) in reaction (2) and (**7a–e**) in reaction (3) (Scheme 2) with respect to **4a–e**. B3LYP/6-311+G** energies in normal text and CCSD(T)/cc-PVDZ//B3LYP/6-311+G** energies (all in kcal mol^{-1}) in bold text. Bird aromaticity indices (BI), nucleus independent chemical shifts (NICS) and ISEc homodesmotic B3LYP/6-311+G** reaction energies (kcal mol^{-1}) for **4a–e**



b: *Y* = S; **c**: *Y* = O; **d**: *Y* = CH$_2$; **e**: *Y* = NH

	Δ*E*	*E*(TS2)	*E*(TS3)	ISEc	BI/NICS
4a	4.7/**5.2**	**87.7**	55.2	−2.6	44/−5.5
4b	−2.3/**−0.9**	**86.0**	49.1	4.4	33/−2.1
4c	−3.6/**−1.9**	**86.1**	51.5	5.7	31/−1.0
4d	−2.4/**−0.5**	**88.6**	46.8	4.5	25/−1.5
4e	−3.2/**−1.6**	**85.4**	51.5	5.3	32/−1.1

The next question was to elucidate what is the driving force of the above isomerisation? Schleyer has recently shown that the energy difference between a conjugated ring with a methyl substituent and its isomer with exocyclic double bonds (termed as isomeric stabilisation energy, ISE) is an excellent measure of aromatic stabilisation, if corrected by the diene *anti–syn* mismatches between the cyclic conjugated system and its isomer.[9] The correction is in fact included in the homodesmotic reaction [see eqn (4)] energy termed here as ISEc. The ISEc results (Table 2) show that σ^3-phosphole **4a** exhibits a slight aromatic stabilization, while all the σ^4-phospholes **4b–e** are slightly antiaromatic!



Y = lone pair (**a**), O (**b**), S (**c**), CH$_2$ (**d**), NH (**e**) (4)

Since the ISEc energies are small, we investigate further aromaticity measures to gather additional evidence about the change in the aromaticity upon P-oxidation of σ^3-phospholes. We selected the Bird indices,[10] a geometric criteria, and the NICS(0),[11] a magnetic criteria. The Bird index of **4a** is considerably larger than for **4b–e** (Table 2). Phosphole **4a** itself has a moderately small negative NICS, while NICS values for σ^4-phospholes[12] **4b–e** are more positive by 3–4 ppm. Hence, both criteria show a similar tendency: σ^3-phosphole **4a** has a small aromaticity, which is shifted towards a small antiaromaticity in the case of σ^4-phospholes **4b–e**. All these data suggest that the inversion of phosphole–phospholene stability upon oxidation of the P-atom is due to an aromatic–antiaromatic switch.

It is noteworthy that the antiaromatic character of the σ^4-phospholes **4b–e** increases with the electronegativity of the Y fragment (Table 2). This behaviour is formally understandable, considering the ylide form of the Y=P bond (↔ Y^-–P^+). The presence of a positively charged phosphorus results in a cyclopentadienide cation-like structure, which is antiaromatic, explaining the destabilization of the σ^4-phospholes. In other words, the positive partial charge at phosphorus, which increases with the increasing electonegativity of the Y substituent, lowers the energy of all orbitals at phosphorus. This prevents the interaction of the endocyclic π-system with the occupied orbitals of the P-fragment, while the interaction with the unoccupied σ^* orbitals (electron demand) is getting more important resulting in an antiaromatic character. This electronic situation is reminiscent of what is observed for 1,1-difluorocyclopentadiene which is also an antiaromatic species.[13] It is also worth mentioning that the aromaticity of the ring carbomers[14] of phosphole and that of phosphole oxide has recently been investigated, and for $C_{14}H_4PH$ a strong antiaromaticity, while for the phosphole oxide $C_{14}H_4P(O)H$ a moderate aromaticity has been observed.

It is clear that the aromaticity of heterocycles such as **A** and **B** (Scheme 1) can be influenced by variation of substituents of the heteroatom. However, the case of the phosphole (aromatic–antiaromatic switch) is unique, even in P-heterocycle chemistry. For example, σ^2-phosphabenzene is highly aromatic, while the σ^4-phosphabenzene was shown to be slightly (with H or alkyl substituent) to significantly (with halogen or OR substituents) aromatic.[3b,15] Thus, variation of substituents reduces but not suppresses aromaticity as illustrated by the fact that σ^4-phosphabenzene derivatives have reduced Wittig-reactivity in comparison with their saturated counterparts,[16] in agreement with an aromatic energetic stabilization.

In conclusion, oxidation of the P-atom of slightly aromatic σ^3-phospholes affords σ^4-derivatives exhibiting a small antiaromatic character. Although this switch in aromatic–antiaromatic stabilisation is small, it has a significant impact on phosphole properties. Firstly it destabilises σ^4-derivatives **2a–d** with respect to their phospholene isomers **3a–d**. Secondly, since the aromatic character of building blocks is a crucial parameter influencing the HOMO–LUMO gap of π-conjugated systems,[17] it is very likely that this aromatic–antiaromatic balance is at the origin of the tuning of optical properties of phosphole-based oligomers upon P-modifications.[4]

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