Benzo-1,3,2-diazaphospholide and Benzo-1,3,2-diazaphospholium: An Isoelectronic Anion-Cation Pair with different Aromaticity

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Supporting Information: Full experimental procedures and characterisation data for **2** and **4**; details on computational studies on **II** (E = P), **III**, **V**, **6**, **7**$^+$, and **8**$^-$.

Synthesis and Characterisation of 2:

THF (0.75 ml) was condensed on a mixture of **1** (80 mg, 0.15 mmol) and sodium (124 mg). After dissolution was complete and the evolution of hydrogen ceased, the mixture was layered with diethyl ether and stored at –20 °C to yield rhombohedral, colourless crystals.

For the synthesis of preparative amounts, the procedure was repeated starting with 1.5 mmol of **1** and the appropriate amount of sodium. The product formed was isolated in up to quantitative yield after evaporation of the solvent. Purification of the isolated product can be accomplished, if necessary, by dissolution in THF and precipitation with diethyl ether.

$^{31}P\{^1H\}$ NMR (THF-d_8): δ = 272.3 (s). – ^{1}H-NMR (THF-d_8): δ = 7.60 (m, 2 H), 6.87 (m, 2 H), 3.66 (m, 8 H, THF), 1.72 (m, 8 H, THF).

$^{13}C\{^1H\}$ NMR (THF-d_8): δ = 153.7 (s), 118.5 (d), 118.1 (d, J_{PC} = 14.4 Hz).

Elemental analysis: Calcd. for $C_{14}H_{20}N_2NaO_2P$ (302.29): C 55.63 H 6.67 N 9.27; found C 54.71 H 6.62 N 8.98.

Synthesis and Characterisation of 4:

Triflic acid (0.33 ml, 3.75 mmol) was added drop wise to a suspension of **1** (400 mg, 3 mmol) in xylene (10 ml). After stirring for 12 h, all volatiles were evaporated under reduced pressure. The residue was extracted three times with diethyl ether and all volatiles were removed under reduced pressure. The remaining colourless powder was spectroscopically pure. A crystalline sample suitable for X-ray diffraction studies was obtained by crystallisation from a saturated solution in diethyl ether at –20 °C; m.p. 165 °C (dec.).

$^{31}P\{^1H\}$ NMR (CD_3CN): δ = 211.9 (s). – ^{1}H NMR (CD_3CN): δ = 8.90 (br s, 2 H, N**H**), 7.88 (m, 2 H), 7.64 (m, 2 H). – $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 127.3 (d, J_{PC} = 1.9 Hz), 115.3 (d, J_{PC} = 1.3 Hz), 126.6 (q, CF_3).

Elemental analysis: no correct elemental analysis could be obtained as the formation of CF_4 during the combustion process lead to erroneous and irreproducible data.

Computational Studies

All computations were carried out with the Gaussian 03 [1] program package. Geometry optimisation was performed by using the B3LYP method [2] with the B3LYP/6-311+G** basis set. At each optimised structure a vibrational analysis was performed to confirm that the stationary point located was a minimum on the potential energy hypersurface.

In order to study the aromaticity of the cation (**V**), the anion (**IIP**) and the neutral benzo-1,3,2-diazaphosphole **III** *NICS*(0), *NICS*(1) values, Bird indices (*BI*) and bond shortening indices (*BDSHRT*) have been determined and energies of tabilisation reactions have been calculated. Gordy bond orders for Bird index [4] and *BDSHRT* [5] were calculated using the Gordy equation ($N = A\,r^{-2} - B$; where N is the bond order, r is the bond distance, A and B are parameters calculated using prototype single and double bonded reference bond distances, e.g. for PN bond using $H_2P{-}NH_2$ and HP=NH). All the geometries were fully optimised at the B3LYP/6-311+G** level of theory. Note that the Gordy constants A and B were determined for neutral molecules. These geometric criteria have been determined for the N and C analogues as well. The larger the *BI* or *BDSTHRT* is, the more aromatic the ring.

The nucleus independent chemical shifts *NICS*(0) and *NICS*(1) [3] (nucleus independent chemical shifts determined at the ring centre and 1 Å above or below it, respectively) are magnetic aromaticity criteria and were calculated at the B3LYP/6-311+G** level. The more negative the *NICS* value is, the more aromatic the ring.

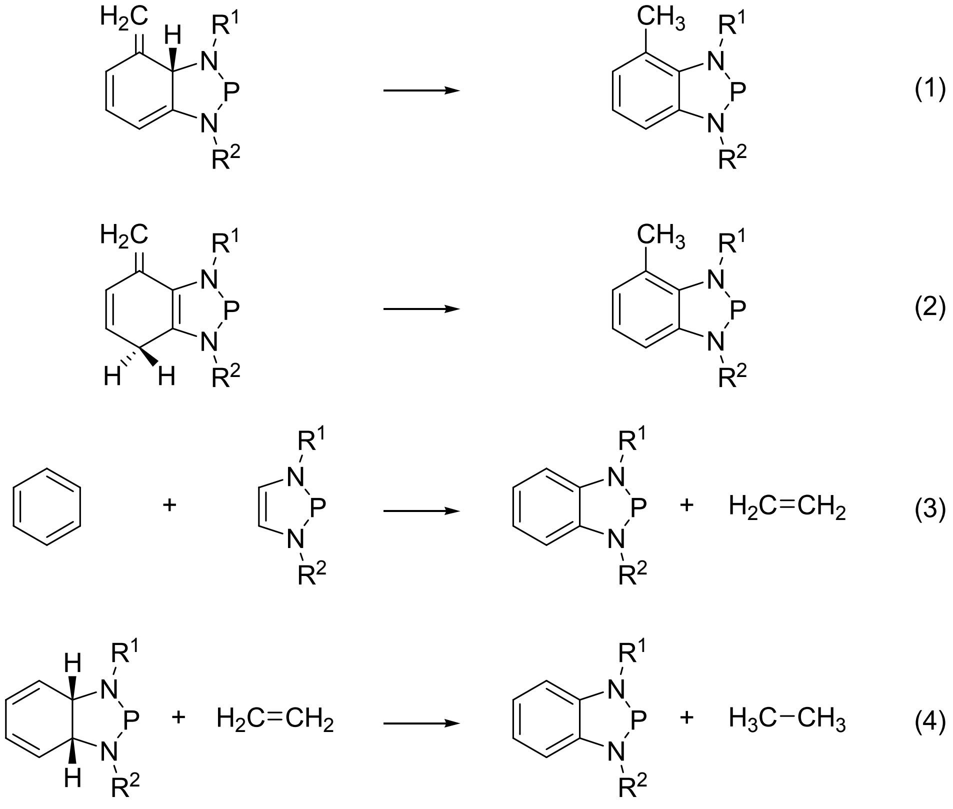
The energetic stabilisation effect of aromaticity has been measured with isodesmic and isomer stabilisation energies. The reactions (3) and (4) are isodesmic reactions that separate fully the ring systems. If these reactions are exothermic, the annulated systems gain stabilisation energy in comparison with the separated systems on the left hand. Similarly, reactions (1) and (2) (isomer stabilisation reaction: ISE) also measure the effect of the conjugation. Reaction

(1) abolishes the cyclic aromatic stabilisation in both rings, while reaction (2) only hampers the cyclic conjugation in the six-membered ring. The more exothermic these reactions are, the larger the aromatic stabilisation. All reaction energies were calculated at the B3LYP/6-311+G** level of theory.

The calculated magnetic and geometric indices for **III**, **V**, and **IIP** (Scheme 1) as well as for benzene as a reference are listed in the table below:

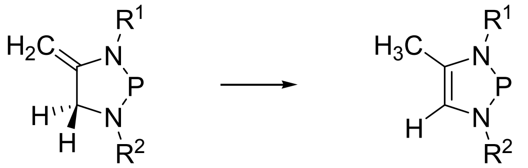
	5 membered ring				6 membered ring			
	NICS(0)	*NICS*(1)	*BI*	*BDSHRT*	*NICS*(0)	*NICS*(1)	*BI*	*BDSHRT*
III	−12.0	−10.9	49	41	−8.8	−10.5	85	59
V	−12.6	−9.9	83	38	−9.5	−11.0	88	61
IIP	−12.2	−13.1	89	41	−7.8	−9.7	78	54
Benzene					−8.0	−10.2	100	62

The reaction energies of the isomerisation stabilisation reactions (1) and (2) and the isodesmic reactions (3) and (4) computed at the B3LYP/6-311+G** level of theory in kcal mol^{-1}:



	R^1	R^2	*ΔE* (1)	*ΔE* (2)	*ΔE*(1)−*ΔE*(2)
6	H	–	−50.8	−23.9	−26.9
7^+	H	H	−49.0	−24.2	−24.8
8^-	–	–	−48.7	−24.5	−24.2
	R^1	R^2	*ΔE* (3)	*ΔE* (4)	
III			7.1	−65.7	
V			3.9	−58.1	
IIP			1.6	−80.3	

The energies of the isomerisation stabilisation reaction (5) of five-membered rings (*ΔE* (5), kcal mol^{-1}, B3LYP/6-311+G**):



(5)

R^1	R^2	*ΔE* (5)
H	H	−25.0
H	–	−25.0
–	–	−28.4

Total energies (in hartrees) and optimised geometrical parameters (in Å) and of III, V and II (E = P) **(B3LYP/6-311+G**)**

III (neutral)
E: −682.6404365

C	1.329737	−1.365260	0.000000
C	2.474560	−0.585218	0.000000
C	2.402516	0.823914	0.000000
C	1.182942	1.475003	0.000000
C	0.000000	0.711134	0.000000
C	0.090572	−0.710728	0.000000
N	−1.281657	1.196562	0.000000
P	−2.372966	0.003277	0.000000
N	−1.178166	−1.245186	0.000000
H	1.391280	−2.447810	0.000000
H	1.112387	2.555861	0.000000
H	3.445519	−1.067190	0.000000
H	3.320503	1.400120	0.000000
H	−1.338405	−2.242843	0.000000

V (cation)
E: −683.0140547

C	0.000000	−0.706746	−2.471290
C	0.000000	−1.431098	−1.294183
C	0.000000	−0.705841	−0.096459
C	0.000000	0.705841	−0.096459
C	0.000000	1.431098	−1.294183
C	0.000000	0.706746	−2.471290
N	0.000000	1.173566	1.205719
P	0.000000	0.000000	2.404737
N	0.000000	−1.173566	1.205719
H	0.000000	2.513964	−1.295779
H	0.000000	−2.513964	−1.295779
H	0.000000	1.233053	−3.417679

H	0.000000	−1.233053	−3.417679
H	0.000000	−2.167821	1.409490
H	0.000000	2.167821	1.409490

II (E = P, anion)

E: −682.0903253

C	0.000000	−0.707560	−2.411304
C	0.000000	−1.417919	−1.221153
C	0.000000	−0.725465	0.010807
C	0.000000	0.725465	0.010807
C	0.000000	1.417919	−1.221153
C	0.000000	0.707560	−2.411304
N	0.000000	1.272524	1.255732
P	0.000000	0.000000	2.335153
N	0.000000	−1.272524	1.255732
H	0.000000	2.503996	−1.215170
H	0.000000	−2.503996	−1.215170
H	0.000000	1.240105	−3.358703
H	0.000000	−1.240105	−3.358703

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