PERKIN 2

Superbasic bridgehead diphosphines: the effects of strain and intrabridgehead P · · · P bonding on phosphine basicity

Roger W. Alder,[*a] **Craig P. Butts,**[a] **A. Guy Orpen,**[a] **David Read**[a] **and Josep M. Oliva**[b]

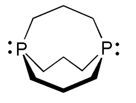
[a] *School of Chemistry, University of Bristol, Bristol, UK BS8 1TS*
[b] *Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., Bellaterra, 08193 Barcelona, Spain*

Received (in Cambridge, UK) 2nd November 2000, Accepted 11th January 2001
First published as an Advance Article on the web 5th February 2001

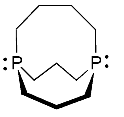
The basicity order in acetonitrile for a series of phosphines is: 1,5-diphosphabicyclo[3.3.3]undecane **1** (pK_a for the protonated ion ~ 17.9) < 1,6-diphosphabicyclo[4.3.3]dodecane **2** (pK_a ~ 22.5) < 1,6-diphosphabicyclo[4.4.3]tridecane **3** (pK_a 27.8). The latter is therefore comparable to Schwesinger's P_1–*t*-Bu base but still significantly weaker than Verkade's proazaphosphatrane bases. The pK_a for the protonated ion of 1,6-diphosphabicyclo[4.4.4]tetradecane **4** could not be determined due to rearrangement probably caused by preferred deprotonation at α-carbon. However, the X-ray structure of **4**H·PF$_6$ ($^1J_{PP}$ 178 Hz) shows an *in,out* structure with a P · · · P distance of 2.58 Å, indicative of significant bonding. Diphosphines **2** and **3** protonate to give *in,out*-**2**H$^+$ ($^1J_{PP}$ 251 Hz) and *in,out*-**3**H$^+$ ($^1J_{PP}$ 253 Hz), but **1**H$^+$ shows no P–P coupling and is believed to be *out,out*. Proton affinities (PA) for the bridgehead diphosphines have been calculated at the B3LYP/6-31G* level: **1**, 1001, **2**, 1040, **3**, 1085, and **4**, 1105 kJ mol^{-1} and are compared with PA[(*t*-Bu)$_3$P] = 1028 kJ mol^{-1}. All the bridgehead diphosphines are strongly flattened and the question of how much this may contribute to their enhanced basicity, in addition to the effect of intrabridgehead bonding, is discussed.

Introduction

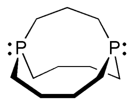
A number of superbasic phosphorus compounds have been reported, in particular the phosphazenes of Schwesinger and Schlemper[1] and Verkade and co-workers' proazaphosphatranes,† *e.g.* **5**,[2] and pK_a values of these have been reported in acetonitrile (data for **5** and for two of Schwesinger's P_1 bases, BTPP and P_1–*t*-Bu,‡ are given in Table 2; pK_a values for compounds with multiple phosphazene units range up to ~47 in the case of P_5–*t*-Bu). The extraordinarily high basicities associated with these species, which far outstrip typical proton sponges, have led to them being increasingly used as bases in synthetic applications. Both Schwesinger and Verkade's compounds undoubtedly benefit from extensive charge dispersal onto the nitrogen atoms. In the case of the proazaphosphatranes, X-ray data show that there are short transannular (or intrabridgehead) P–N distances of 2.07 Å, but how much this contributes to the enhanced basicity remains to be clarified.



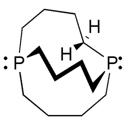
out,out-**1**



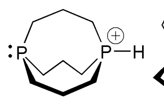
out,out-**2**



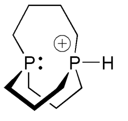
out,out-**3**



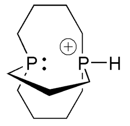
out,out-**4**



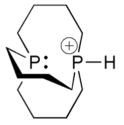
out,out-**1**H$^+$



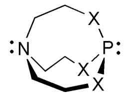
in,out-**2**H$^+$



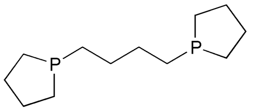
in,out-**3**H$^+$



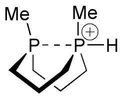
in,out-**4**H$^+$



5, X = NMe



6



7

We have been engaged for some time in studying the chemistry of bridgehead medium-ring diphosphines and their derivatives,[3] partly for comparison with their diamine counterparts which we studied earlier.[4,5] We have reported the preparation of 1,5-diphosphabicyclo[3.3.3]undecane **1**,[6] 1,6-diphosphabicyclo[4.3.3]dodecane **2**,[7] and 1,6-diphosphabicyclo-[4.4.3]tridecane **3**,[3] but found that although the protonated ion of 1,6-diphosphabicyclo[4.4.4]tetradecane **4** could be made, all attempts at deprotonation lead to deep-seated rearrangements, probably initiated by deprotonation at α-carbon (see later).[3] This suggested that these diphosphines were extremely strong bases, even though they do not possess any conventional means of charge dispersal. In this paper, we report our investigation into the basicity of these compounds, and seek to understand the factors responsible.

Results and discussion

The basicity of trialkylphosphines

The most basic simple phosphines are tri-*tert*-butylphosphine[8] and tris(2,4,6-trimethoxyphenyl)phosphine[9] which are reported to have aqueous pK_a values of 11.4 and 11.2 respectively. Both have recently found applications as highly basic and sterically hindered ligands in transition metal catalysed processes.[10] The high pK_a values in these cases are rationalised by strain relief, with a contribution from increased electron donation to phosphorus from the electron-rich substituents. Typical trialkylphosphines have small C–P–C angles (~100°), whereas phosphonium cations are (approximately) tetrahedral. Thus when C–P–C angles in the phosphine are increased by nonbonding interactions, there is relief of angle strain on

---

† Atranes are 1,5-diheteroatom derivatives of bicyclo[3.3.3]undecane with some type of bonding interaction between the two bridgehead atoms; proazaphosphatranes are derivatives of 2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane.

‡ The IUPAC names for BTPP and P_1–*t*-Bu are *tert*-butylimino-(tripyrrolidino)-λ^5-phosphane and *tert*-butylimino[tris(dimethylamino)]-λ^5-phosphane, respectively.

Table 1 Proton affinity of PH_3 as a function of pyramidality from B3LYP/6-31G* calculations

H–P–H angle/°[a]	PH_3 energy/ E_h[b]	PH_4^+ energy/ E_h[b]	Proton affinity (PA)/kJ mol^{-1}[c]
80.0	−343.10208	−343.34461	637
85.0	−343.10906	−343.36321	667
90.0	−343.11288	−343.37877	698
95.0	−343.11343	−343.39134	730
100.0	−343.11051	−343.40080	762
105.0	−343.10382	−343.40681	795
110.0	−343.09314	−343.40871	829
115.0	−343.07881	−343.40468	856

[a] C_{3v} symmetry maintained throughout. [b] Including thermal corrections at $P = 1$ atm and $T = 298$ K; thermochemistry calculations used frequencies scaled by 0.9804. [c] Proton affinities (PA) = E_{min}(neutral) − E_{min}(protonated).

protonation. In support of this, we have calculated the proton affinity (PA) of PH_3 as a function of pyramidality at the B3LYP/6-31G* level while maintaining C_{3v} symmetry (Table 1). It can be seen that PA increases substantially and almost linearly with C–P–C angle, even beyond tetrahedral.

The effect of solvent on pK_a values

We were unable to study the protonation behaviour of the bicyclic diphosphines in aqueous solvents due to their poor solubility in water and the fact that the protonated ions *in,out*-$2H^+$ and *in,out*-$3H^+$ are instantly hydrolysed to a variety of products (^{31}P NMR spectroscopy). While there are established pK_a scales in DMSO[11] and THF,[12] DMSO readily oxidises bicyclic diphosphines and THF is a poor solvent for the protonated ions. Schwesinger and co-workers have determined a useful pK_a scale in acetonitrile,[13,14] hence this was the solvent of choice for our studies.

The protonation of simple trialkylphosphines has not been widely studied in acetonitrile, although the pK_a of the conjugate acid of tri-*tert*-butylphosphine has recently been reported as 17 in this solvent.[12] The pK_a values for a number of alkyl- and arylphosphines have been determined in nitromethane,[15,16] a solvent with rather similar relative permittivity and basicity. The pK_a value for the protonation of Et_3P, the most basic of the trialkylphosphines studied, is 15.49 in this solvent,[16] which corresponds to a pK_a of *ca.* 15.6 in acetonitrile.[14] This compares with a pK_a value of 18.46 for Et_3N[17] and shows the phosphine to be a considerably weaker base than the amine.

While pK_a values on the acetonitrile scale tend to be between 7 and 13 units higher than on the aqueous scale, the actual difference for any given acid cannot be accurately predicted. Coetzee listed the pK_a values for a number of acids showing the wide variation between their aqueous and acetonitrile values (ΔpK_a);[18] the unique properties of water as a solvent are undoubtedly responsible for the apparently anomalous ΔpK_a values at the extremes.

The basicities of bicyclic diphosphines

1,6-Diphosphabicyclo[4.4.3]tridecane 3. Initial investigations were based on the treatment of $3H^+$ with a range of bases in order to estimate its pK_a. It was found that DBU did not cause deprotonation, whilst Schwesinger's P_2–Et base, which has a pK_a close to Verkade's atrane **5**, led to complete deprotonation giving **3**. However, treatment of $3H^+$ with one equivalent of Schwesinger's P_1–*t*-Bu base led to partial deprotonation. The ratio of $3H^+:3$ as measured by ^{31}P NMR spectroscopy, was close to 7.5 : 1, indicating that [4.4.3]-diphosphine **3** is a stronger base than the P_1–*t*-Bu base. The position of equilibrium was confirmed by performing the reaction in the reverse direction. In this case, the free diphosphine **3** was treated with one equivalent of the triflate salt of the P_1–*t*-Bu base ([P_1–*t*-Bu]-H·CF_3SO_3) and ^{31}P NMR spectroscopy showed that the same equilibrium mixture of $3H^+:3$ had been established. These results correspond to the protonated salt $3H^+$ having a pK_a of 27.8 in acetonitrile.

To confirm this result, $3H^+$ was treated with Schwesinger's BTPP base, a derivative of the P_1 base with a pK_a of 28.35. Once again, ^{31}P NMR spectroscopy showed that an equilibrium mixture of $3H^+:3$ had been formed, this time the free diphosphine predominating by a factor of 7 : 3. This was again a reproducible figure and also corresponds to a pK_a for $3H^+$ of 27.8 in acetonitrile.

1,6-Diphosphabicyclo[4.3.3]dodecane 2. Preliminary investigations involved the treatment of $2H^+$ with a number of bases. Treatment with triethylamine led to no deprotonation, but both P_1–*t*-Bu base and DBU led to complete deprotonation giving **2**. Throughout these experiments, we have assumed that the minimum relative concentration of a given species that one may measure by ^{31}P NMR spectroscopy is 2%. Bearing this in mind, and the fact that the pK_a of [DBU]H^+ is 24.13,[19] we can place an upper limit on the pK_a of **2** of 22.44.

At this point, it became more convenient to consider the addition of suitable weak acids to [4.3.3]-diphosphine **2**, since bases whose conjugate acids have appropriate pK_a values were not readily available. ^{31}P NMR spectroscopy showed that treatment of **2** with ethyl nitroacetate (pK_a in acetonitrile ~ 20)[13] led to complete proton transfer, giving $2H^+$. Treatment of **2** with one equivalent of $(PhSO_2)_2CH_2$ and subsequent analysis by ^{31}P NMR spectroscopy showed that an equilibrium mixture of **2** and $2H^+$ was generated, with $2H^+$ predominant by a factor of 3 : 2. Unfortunately, the pK_a of $(PhSO_2)_2CH_2$ is only known approximately (pK_a in acetonitrile ~ 22.5),[13] and so we can only assert that the pK_a of $2H^+$ is close to 22.5, in keeping with the observations in the treatment of **2** with DBU.

1,5-Diphosphabicyclo[3.3.3]undecane 1. In the case of **1**, proton exchange in the presence of suitable acids was evidently more rapid than that observed with the larger ring systems, resulting in broad, averaged peaks for the bicyclic species in the ^{31}P NMR spectra. This averaging means that the NMR integration method employed previously cannot be used, but information can be derived from the chemical shift changes observed in the ^{31}P NMR spectra of mixtures of [3.3.3]-diphosphine **1** and acidic species.

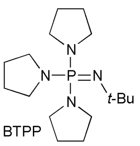
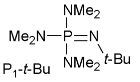
One equivalent of trifluoroacetic acid was added to diphosphine **1**, and subsequent analysis by ^{31}P NMR spectroscopy showed a single broad peak at *ca.* −6 ppm, whilst addition of triethylammonium trifluoroacetate ($Et_3NH{\cdot}CF_3CO_2$) to **1** led to a species exhibiting a single broad peak at *ca.* −23 ppm. Free diphosphine **1** had a single sharp resonance at −27.5 ppm, so it appears that, from the chemical shift differences, approximately 20% proton transfer from triethylammonium trifluoroacetate to diphosphine **1** occurred. These results were reproducible and the NMR spectra of these mixtures remained unchanged over a period of days and were unchanged by dilution, implying a pK_a of *ca.* 17.9 for $1H^+$.

Tri-*tert*-butylphosphine. As discussed previously, tri-*tert*-butylphosphine is the most basic trialkylphosphine known, its conjugate acid having aqueous and acetonitrile pK_a values of 11.4 and 17.0 respectively. To see if our diphosphines are more powerful bases than $(t\text{-Bu})_3P$, each bicyclic diphosphine was treated with one equivalent of $(t\text{-Bu})_3PH{\cdot}CF_3CO_2$. Analysis by ^{31}P NMR spectroscopy showed that both $2H^+$ and $3H^+$ were formed rapidly and quantitatively in the experiments involving their parent diphosphines. When **1** was treated with $(t\text{-Bu})_3PH{\cdot}CF_3CO_2$, the broad peaks observed in the ^{31}P NMR spectrum indicated the formation of an equilibrium mixture of species with ΔpK_a < 1 unit, but did not permit a reliable ΔpK_a to be deduced. Nevertheless, these observations are consistent with the estimate made above for the pK_a of $1H^+$.

The results are compiled in Table 2, together with pK_a values for the other species discussed.

Deprotonation of 4H·OTf. Initial attempts to prepare 1,6-diphosphabicyclo[4.4.4]tetradecane **4** by treatment of **4**H·OTf with *n*-butyllithium led to the formation of the remarkable rearranged product **6**.[3] The mechanism of this rearrangement has not been elucidated, but probably involves C-deprotonation, and transfer of the ylidic carbon to the other phosphorus atom. Other bases gave **6** and another material in varying proportions. ^{31}P NMR of the second product shows a chemical shift 72.7 ppm with $^1J_{PH} = 202$ Hz, typical of a secondary phosphine, but we have been unable to isolate this product in sufficient purity to determine its structure.

Table 2 pK_a (or pK_{BH^+}) in acetonitrile at 25 °C

Acid or base	pK_a
Atrane **5**	32.8[30]
 BTPP	28.35[31]
3	27.8
 $Me_2N{-}P({=}N{-}t\text{-}Bu)(NMe_2)_2$ P$_1$-*t*-Bu	26.89[1]
DBU	24.13[19]
2	*ca.* 22.5
$(PhSO_2)_2CH_2$	*ca.* 22.5[13]
$EtOCOCH_2NO_2$	*ca.* 20.0[13]
Et_3N	18.46[17]
1	*ca.* 17.9
(*t*-Bu)$_3$P	17.0[12]
Et_3P	15.6[14]

Calculation of the proton affinities of 1–4 and (*t*-Bu)$_3$P

We have calculated the proton affinities of diphosphines **1**–**4** and (*t*-Bu)$_3$P, using the B3LYP density functional with the 6-31G* basis set; thermochemistry calculations used frequencies scaled by 0.9804. In general the results, summarised in Table 3, run nicely parallel to our pK_a results, in that there is clearly a substantial increase in both PA and pK_a as *in*,*out*-structures and P–P bonding come into play. It is noticeable that the PA of **1** is calculated to be lower than that of (*t*-Bu)$_3$P, although we are suggesting a higher pK_a in solution. It seems possible that solvation of (*t*-Bu)$_3$PH$^+$, especially any hydrogen bonding, would be inhibited by steric hindrance, which should be much less severe for **1**H$^+$.

The structure of bicyclic diphosphines 1, 2 and 3

In order to understand the high basicities of the bridgehead diphosphines, knowledge of their structure (and of their protonated ions) is required. The structure of **1** has been reported and it shows average C–P–C angles of 105.7° (Table 4),[3] representing considerable flattening relative to unstrained trialkylphosphines. Attempts to obtain structural data for **2** or **3** failed, although enlarged C–P–C angles are partially supported by ^{31}P NMR chemical shifts. Flattened phosphines exhibit downfield shifts due to the reduced degree of s-character in the orbital carrying the lone pair[20] and the chemical shifts of **2** and **3** (25.24 and 21.53 ppm respectively in C_6D_6) are indeed downfield relative to **1** (30.07 ppm in C_6D_6). Of course the different connectivity of these bicyclic systems could have some influence, but the trend is certainly in the expected direction. B3LYP/6-31G* density functional calculations (Table 4) also support large C–P–C angles in **2** and **3**, although the calculated trend is to smaller angles in the larger systems, perhaps due to greater conformational flexibility (the lowest energy conformer for **4** lacks any symmetry and has one α-C–H group tipped inside the cage as an alternative way of relieving the strain in the bridges).

Table 3 Proton affinities for phosphines

	Symmetry	B3LYP/6-31G* energy/E_h [a]	B3LYP + Thermal corrections/E_h [b]	Proton affinity (PA)/kJ mol^{-1} [c]
P[3.3.3]P, **1**				1001
out,*out*	C_{3h}	−1036.48192	−1036.21660	
out,*out*-H$^+$	C_3	−1036.87435	−1036.59782	
P[4.3.3]P, **2**				1040
in,*out*		−1075.74134	−1075.44897	
out,*out*		−1075.77793	−1075.48326	
in,*out*-H$^+$		−1076.18425	−1075.87919	
out,*out*-H$^+$		−1076.17358	−1075.86745	
P[4.4.3]P, **3**				1085
in,*out*		−1115.06265	−1114.74029	
out,*out*		−1115.07685	−1114.75203	
in,*out*-H$^+$		−1115.50037	−1115.16531	
out,*out*-H$^+$		—	—	
P[4.4.4]P, **4**				1105
out,*out*	D_3	—	—	
out,*out* [d]		−1154.38561	−1154.03122	
in,*out* [e]	C_3	—	—	
in,*out*-H$^+$	C_3	−1154.81665	−1154.45203	
out,*out*-H$^+$		—	—	
(*t*-Bu)$_3$P				1028
(*t*-Bu)$_3$P	C_3	−814.87557	−814.49325	
(*t*-Bu)$_3$PH$^+$	C_3	−815.27829	−814.88483	

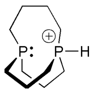
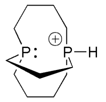
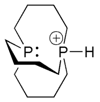
[a] All optimised geometries correspond to energy minima. [b] Thermal corrections at $P = 1$ atm and $T = 298$ K; thermochemistry calculations used frequencies scaled by 0.9804. [c] Proton affinities refer to the most stable neutral and protonated species: PA = E_{min}(neutral) − E_{min}(protonated). [d] The optimised geometry lacks any symmetry and has one C–H bond tipped inside the cage. [e] The best *in*,*out*-conformation was less stable than the lowest energy *out*,*out*.

Table 4 Selected structural data for **1**, **2**, **3**, and **4** and their protonated ions from X-ray determinations and B3LYP/6-31G* density functional calculations

	Method	P–P distance/Å	P–H distance/Å	C–P–C/°	C–P(H)–C angle/°	Average C–C–C angle/°
out,*out*-**1**[a]	X-Ray	4.07	—	106.4, 105.1, 106.0, 106.4, 105.4, 105.0	—	
out,*out*-**1**	B3LYP/6-31G*	4.13	—	105.5 (all equal)	—	118.7 (all equal)
out,*out*-**1**H^+	B3LYP/6-31G*	3.77	1.41	106.4 (all equal)	114.7 (all equal)	117.6 (all equal)
out,*out*-**2**[b]	B3LYP/6-31G*	4.39	—	107.1 (av.)	—	117.8 (av.)
in,*out*-**2**H^+[b]	B3LYP/6-31G*	2.55	1.44	113.1 (av.)	119.4 (av.)	114.7 (av.)
out,*out*-**3**	B3LYP/6-31G*	4.48	—	105.8 (av.)	—	118.3 (av.)
in,*out*-**3**H^+	B3LYP/6-31G*	2.70	1.43	109.8 (av.)	119.3 (av.)	115.3 (av.)
out,*out*-**4**	B3LYP/6-31G*	4.98	—	103.8 (av)	—	116.0 (av.)
in,*out*-**4**H^+	X-Ray	2.58		106.3, 106.6, 107.8	118.2, 119.4, 119.5	115.4
in,*out*-**4**H^+	B3LYP/6-31G*	2.72	1.43	107.0 (all equal)	119.0 (all equal)	116.2 (av.)

[a] Ref. 3. [b] Ref. 7.

Table 5 Spectroscopic data for *in*,*out*-**2**H^+ and *in*,*out*-**3**H^+ and *in*,*out*-**4**H^+

Compound		δ_P (P*P*H) (ppm)	δ_P (*P*PH) (ppm)	$^1J_{PP}$/Hz	$^1J_{PH}$/Hz	$^2J_{PH}$/Hz[a]	ν_{P-H}/cm^{-1}
	**2**H^+	−27.18	−17.87	251	279	83	2352
	**3**H^+	−82.56	−34.93	249	295	106	2152
	**4**H^+	−83.08	−12.33	178	305	112	2175

[a] The sign of $^2J_{PH}$ is unknown.

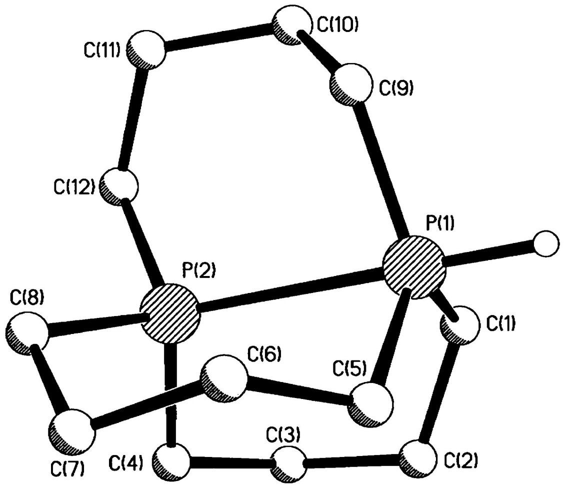


Fig. 1 X-Ray structure of 6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane hexafluorophosphate **4**H·PF_6.

The structure of protonated ions 1H^+–4H^+

We do not have structural data for the protonated ions of **1**, **2** or **3**, but an X-ray determination has been performed on **4**H·PF_6. Important data relating to this structure are listed in Table 4, and the structure is illustrated in Fig. 1. The short P–P distance and the large C–P–C angles at the protonated centre are striking features of the structure. The almost trigonal bipyramidal geometry at the P(H) centre permits close approach of the *in*-phosphine. The P–P distance in this structure is much closer to those of normal P–P single bonds (2.1–2.2 Å) than to twice the van der Waals radius of phosphorus (3.8 Å), although actual P–P bonding may be quite weak (see below).

The evidence from NMR spectroscopy indicates that the protonated ions *in*,*out*-**2**H^+ and *in*,*out*-**3**H^+ exist in similar *in*,*out* conformations to **4**H^+. The protonated salt of **1** cannot be isolated as a discrete species, but the broad peaks observed in the presence of one equivalent of trifluoroacetic acid indicate rapid proton exchange between *out*,*out* species. We have obtained crystal structures of other adducts in the [4.4.4] and [4.4.3] series,[21] and *in*,*out* conformations are always associated with substantial J_{PP} couplings in ^{31}P NMR (but there is no simple relationship between P–P distance and J_{PP}), whereas unsymmetrical *out*,*out* derivatives (mainly in the [4.4.3] and [4.3.3] series) show no P–P coupling.

The B3LYP/6-31G* calculated structure for *in*,*out*-**4**H^+ agrees reasonably well with the X-ray data. By far the largest discrepancy lies in the calculated P–P distance (0.14 Å longer); stretching this (probably weak) bond may be quite inexpensive energetically. The calculated P–P distances (Table 4) for *in*,*out*-**2**H^+ and *in*,*out*-**3**H^+ should therefore be treated with some caution.

In their report on the basicity of tri-*tert*-butylphosphine and other phosphines, Allman and Goel indicated that the magnitude of P–H coupling constants ($^1J_{PH}$) decreased with increasing phosphine basicity.[8] However, whereas typical protonated phosphines have coupling constants of 450–600 Hz, values in our systems are considerably smaller (*ca.* 300 Hz). This is presumably because the hybridisation at the protonated phosphorus in ions **2**H^+–**4**H^+ is quite different to that in normal protonated trialkylphosphines. Spectroscopic data for *in*,*out* protonated ions **2**H^+–**4**H^+ (see Table 5) show that the magnitudes of $^1J_{PH}$ and $^2J_{PH}$ actually increase with increasing basicity. In the case of $^2J_{PH}$ we are uncertain as to whether these

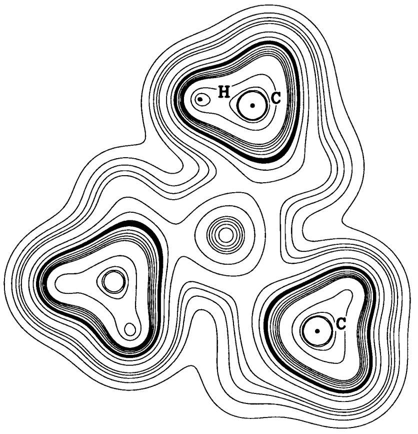


Fig. 2 Contour map of the electron density for $3H^+$ in the plane defined by the two vectors of negative curvature of the density and containing the bond critical point between the two phosphorus atoms.

couplings are positive or negative. The $\nu_{P\text{–}H}$ values show no clear trend, but are rather lower than for typical protonated phosphines, suggesting weaker P–H bonds. In their reactivity, these P–H groups show some hydridic character.[21]

Factors contributing to the high basicity of bicyclic diphosphines

The enhanced basicity of **1** compared with Et_3P is surely mostly due to enlarged C–P–C angles. The similar angles calculated for **2**–**4** suggest that these diphosphines would also have pK_a values of around 18 in acetonitrile, were it not for the effect of the transannular P–P interaction. The PA values calculated for **2**–**4** are much higher than could be accounted for by the extra methylene groups present (a typical increment is ≤5 kJ mol^{-1} per CH_2). The almost linear correlation of pK_a with calculated PA values suggests a pK_a ~ 30 for $4H^+$, approaching the value for Verkade's proazaphosphatrane **5**.

It seems clear that $2H^+$–$4H^+$ are substantially stabilised by some other effect, perhaps by as much as 90 kJ mol^{-1} in the case of $4H^+$. However it is far from obvious whether this is strain relief on protonation, the altered hybridisation at the P(H), the transannular P–P interaction, or a combination of all these. The fact that we do not see the formation of related ions like **7** in the protonation of monocyclic medium-ring diphosphines, suggests that the P–P interaction is not strong. In the intrabridgehead situation there is likely to be significant strain relief on bringing the two phosphorus atoms together, whereas in the monocyclic case any relief of transannular non-bonded interactions may be countered by close approach of the methyl groups in **7**.

We have sought to clarify the extent of P–P bonding from the density functional calculations. A Bader atoms-in-molecules analysis[22] shows that there is a bond critical point[23] between the phosphorus atoms in $3H^+$, corresponding to a maximum in the electron density of 0.05 electron $bohr^{-3}$ (see Fig. 2) in the plane defined by the axes of negative curvature (of the electron density), and a minimum along the axis of positive curvature (the $P\cdots P$ direction). Thus there is definitely bonding between the phosphorus atoms. The distances between the protonated and unprotonated P atoms and the bond critical point (r_c) are respectively $R(PH^+ - r_c)$ = 1.228 Å and $R(P - r_c)$ = 1.467 Å. For comparison, the electron density at the bond critical point in H_2P–PH_2 (P–P distance 2.25 Å) is over twice as large (0.11 electron $bohr^{-3}$). The total electron density shows some extension of the "lone pair" electron density on the *in*-P towards the protonated phosphorus, but that this is far less that the electron density in the region of the P–H bond. Thus it seems to us that the actual P–P bonding may be relatively weak, even possibly energy-neutral, but that approach of the P atoms provides an effective means of strain relief. Whatever the true situation, the overall effect on the pK_a and PA of these phosphines is a very striking increase in basicity.

Conclusions

Bridgehead diphosphine **1** (pK_a ~ 17.9 in CH_3CN) is comparable in basicity to the most basic simple phosphine, $(t\text{-Bu})_3P$ (pK_a ~ 17.0), and this is largely due to the effects of enlarged C–P–C angles. Diphosphines **2** and **3** are significantly stronger bases (pK_a ~ 22.5 and 27.8 respectively), and this is associated with formation of an *in*,*out*-protonated ion, but it is not clear if the strongly enhanced basicity is due to strain relief on protonation, the altered hybridisation at the P(H), the transannular P–P interaction, or a combination of all these. Diphosphine **4** is predicted to be an even stronger base (pK_a ~ 30), but cannot be obtained from $4H^+$, due to rearrangement on deprotonation.

Experimental

All solvents were purified according to literature procedures[24] and all reactions were carried out under dry nitrogen. All NMR spectra were recorded on a JEOL JNM-GX400 NMR spectrometer. ^{31}P NMR Spectra are referenced externally to 85% H_3PO_4.

Compounds **1**–**3**, their protonated salts, and $4H\cdot PF_6$ were prepared according to our previously published procedures.[3,7] Tri-*tert*-butylphosphine was purchased from Strem Chemicals and its protonated salt prepared by the addition of one equivalent of trifluoroacetic acid to a solution of the phosphine in acetonitrile. Schwesinger's phosphazene bases (P_1–*tert*-butyl and BTPP) were purchased from Fluka Chemicals and their protonated salts prepared by the addition of one equivalent of trifluoroacetic acid to a solution of the phosphazene in acetonitrile. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Lancaster Chemicals and its protonated salt prepared as above. Except where stated, all pK_a values are quoted in acetonitrile.

pK_a Determinations

General method for the treatment of bicyclic diphosphines with suitable acids. A solution of the acid (*ca.* 0.03 mmol) in CD_3CN (*ca.* 50 μL) was added to a solution of the diphosphine (*ca.* 0.03 mmol; 1 eq.) in CD_3CN (500 μL) in an NMR tube. ^{31}P NMR spectroscopy (162 MHz) was used to evaluate the degree of proton transfer. In cases where equilibria were observed, the spectrum was run with a pulse delay of 10 seconds to ensure the accuracy of the integrals.

General method for the treatment of protonated salts of bicyclic diphosphines with suitable bases. A solution of the base (*ca.* 0.03 mmol) in CD_3CN (*ca.* 50 μL) was added to a solution of the protonated salt of the diphosphine (*ca.* 0.03 mmol; 1 eq.) in CD_3CN (500 μL) in an NMR tube. ^{31}P NMR spectroscopy (162 MHz) was used to evaluate the degree of proton transfer as described above.

Theoretical methods

All calculations were performed with the Gaussian98 suite of programs.[25] The theoretical model used, denoted as B3LYP/6-31G*, is based on density functional theory (DFT) with Becke's three parameter exchange functional[26] and the Lee–Yang–Parr correlation functional,[27,28] and the 6-31G* basis set, which is of double-ζ type and contains an additional set of polarization functions on all atoms, except hydrogens. All optimised molecular geometries are minima in the potential energy hypersurface (a frequency calculation on each optimized geometry resulted in no imaginary frequencies). Molecules such

Table 6 Summary of single crystal X-ray diffraction data for **4H**$^+$·PF$_6$

Formula	$C_{12}H_{25}F_6P_3$
Formula weight	376.23
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	7.8764(9)
b/Å	13.878(2)
c/Å	15.138(2)
V/Å^3	1654.8(3)
Z	4
μ/mm^{-1}	0.409
Temperature/K	173(2)
Measured reflections	10631
Independent reflections	3771
R_{int}	0.0277
R	0.0254

as **1**–**4**, (t-Bu)$_3$P and their protonated species have very flat potential energy hypersurfaces with respect to certain degrees of freedom (nuclear displacements). In order to obtain optimized geometries in all molecules, tolerances for the first derivative of the energy with respect to nuclear displacements and estimated nuclear displacements were therefore set to 1/600 hartree bohr^{-1} (radian) and 4/600 hartree bohr^{-1} (radian) respectively.

X-Ray diffraction studies

X-Ray crystallographic studies were conducted using a Siemens SMART diffractometer at 173 K using graphite monochromated Mo-Kα radiation. Structure solution and refinement were performed using SHELXTL software.[29] The data collected for **4H**·PF$_6$ are summarised in Table 6.§

Acknowledgements

We thank EPSRC for a studentship to D. R. and for support under grants GR/K76160 and GR/L80515. J. M. O. acknowledges the Ministerio de Educación y Cultura (Spain) for a contract under the Programa de Incorporación de Doctores y Tecnólogos.

References

1 R. Schwesinger and H. Schlemper, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1167.
2 J. Tang, J. Dopke and J. G. Verkade, *J. Am. Chem. Soc.*, 1993, **115**, 5015.
3 R. W. Alder, D. D. Ellis, R. Gleiter, C. J. Harris, H. Lange, A. G. Orpen, D. Read and P. N. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1657.
4 R. W. Alder, *Tetrahedron*, 1990, **46**, 683.
5 R. W. Alder, *Chem. Rev.*, 1989, **89**, 1215.
6 R. W. Alder, D. D. Ellis, A. G. Orpen and P. N. Taylor, *Chem. Commun.*, 1996, 539.
7 R. W. Alder and D. Read, *Angew. Chem., Int. Ed.*, 2000, **39**, 2879.
8 T. Allman and R. G. Goel, *Can. J. Chem.*, 1982, **60**, 716.
9 M. Wada, S. Higashizaki and A. Tsuboi, *J. Chem. Res. (S)*, 1985, 38; M. Wada, S. Higashizaki and A. Tsuboi, *J. Chem. Res. (M)*, 1985, 0467.
10 G. C. Fu and A. F. Littke, *Angew. Chem., Int. Ed.*, 1998, **37**, 3387; G. C. Fu and A. F. Littke, *Angew. Chem., Int. Ed.*, 1999, **38**, 2411; G. C. Fu and A. F. Littke, *J. Org. Chem.*, 1999, **64**, 10; K. H. Shaugnessy, P. Kim and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 2123; M. Kawatsura and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 1473; J. P. Wolfe and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 1999, **38**, 2413; R. A. Singer and S. L. Buchwald, *Tetrahedron Lett.*, 1999, **40**, 1095.
11 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.
12 K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2000, **122**, 9155.
13 R. Schwesinger, *Nachr. Chem. Tech. Lab.*, 1990, **38**, 1214.
14 R. Schwesinger, H. Schlemper, C. Hasenfratz, J. Willaredt, T. Dambacher, T. Breuer, C. Ottaway, M. Fletschinger, J. Boele, H. Fritz, D. Putzas, H. W. Rotter, F. G. Bordwell, A. V. Satish, G. Z. Ji, E. M. Peters, K. Peters, H. G. von Schnering and L. Walz, *Liebigs Ann. Chem.*, 1996, 1055.
15 C. A. Streuli, *Anal. Chem.*, 1960, **32**, 985.
16 B. A. Korolev and B. I. Stepanov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1968, **11**, 1193.
17 J. F. Coetzee and C. I. R. Padmanabhan, *J. Am. Chem. Soc.*, 1965, **87**, 5005.
18 J. F. Coetzee, *Prog. Phys. Org. Chem.*, 1967, **4**, 45.
19 I. Kaljurand, T. Rodima, I. Leito, I. A. Koppel and R. Schwesinger, *J. Org. Chem.*, 2000, **65**, 6202.
20 V. Mark, C. H. Dungan, M. V. Crutchfield and J. R. van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.
21 R. W. Alder, C. P. Butts, A. G. Orpen and D. Read, *J. Chem. Soc., Perkin Trans. 2*, 2000, (DOI: 10.1039/b009007g).
22 R. F. W. Bader, in *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1994.
23 The bond critical point (bcp) calculation and the contour map of the electron density at the bcp in the plane defined by the axes of negative curvature (showing the density maximum) was computed with the program Xaim: X Atoms in Molecules Interface, developed by J. C. Ortiz and C. Bo, Universitat Rovira i Virgili, Tarragona, Spain.
24 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, 1996.
25 Gaussian 98, M. J. Frisch, W. G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andrés, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
26 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
27 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
28 B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
29 SHELXTL, Bruker AXS, 1997.
30 P. B. Kisanga, J. Verkade and R. Schwesinger, *J. Org. Chem.*, 2000, **65**, 5431.
31 R. Schwesinger, *Chem. Ber.*, 1994, **127**, 2435.

---

§ CCDC reference number 152495. See http://www.rsc.org/suppdata/p2/b0/b008903f/ for crystallographic files in .cif format.