On the energetics of P–P bond dissociation of sterically strained tetraamino-diphosphanes†

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The homolytic P–P bond fission in a series of sterically congested tetraaminodiphosphanes (R2N)2P−P−(NR)2, two of which were newly synthesized and fully characterized into dianimophosphanyl radicals (R2N)2P+.45−9 was monitored by VT EPR spectroscopy. Determination of the radical concentration from the EPR spectra permitted to calculate free dissociation energies ΔG^Diss as well as dissociation enthalpies ΔH^Diss and entropies ΔS^Diss, respectively. Large positive values of ΔG^Diss indicate that the degree of dissociation is in most cases low, and the concentration of persistent radicals – even if they are spectroscopically observable at ambient temperature – remains small. Appreciable dissociation was established only for the sterically highly congested acyclic derivative (9).2 Analysis of the trends in experimental data in connection with DFT studies indicate that radical formation is favoured by large entropy contributions and the energetic effect of structural relaxation (geometrical distortions and conformational changes in acyclic derivatives) in the radicals, and disfavoured by attractive dispersion forces. Comparison of the energetics of formation for CC-saturated N-heterocyclic diphosphanes and the 7π-radical 3c indicates that the effect of energetic stabilization by π-electron delocalization in the latter is visible, but stands back behind those of steric and entropic contributions. Evaluation of spectroscopic and computational data indicates that dianimophosphanyl radicals exhibit, in contrast to aminophosphonium cations, no strong energetic preference for a planar arrangement of the (R2N)2P unit.

Introduction

Kinetic stabilisation by sterically demanding substituents is an immensely useful concept which has played a key role in the advancement of modern organometallic and molecular inorganic chemistry and permitted the preparation of many new classes of isolable or persistent compounds.1 A distinct example of previously unknown, kinetically stabilised species in main-group element chemistry are long-lived neutral pnictyl radicals R2E− (E = P, As).2 The first specimens, 1 and 2 (Scheme 1), were generated in 1976 by Lappert et al. via reduction of chlorophosphane or chloroarsane precursors and identified as persistent radicals with half-lives \( t_{1/2} > 1 \) month at 20 °C by EPR spectroscopy.3 Building on this pioneering work, to date arsanyl and phosphanyl radicals with a wider selection of bulky alkyl, aryl or amino substituents have been characterized.45

Apart from some recent reports on stable phosphanyl radicals that were isolated and fully characterized in the crystalline state,45 the monomers exist generally only in the gas phase or in solution but are dimerized when solid.45 In several cases, temperature dependent equilibria between phosphanyl radicals and their dimers (Scheme 1) were detected spectroscopically in solution, and the observed prevalence of diphenanes at low temperatures was interpreted as reflecting the

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†Electronic supplementary information (ESI) available: Experimental and simulated EPR spectra of 6–9; plot of computed hyperfine couplings vs. skew angles; \(^1\)H NMR spectra of 9/9; results and evaluation of VT EPR measurements; energies and coordinates of calculated molecular structures of radicals 4–9 and diphosphanes (4)–(9); graphical representation of the structural relaxation; crystallographic data. CCDC 1414814 (9_C1), 1414815 (8), and 1414816 (9). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02854j
gain in enthalpy and the loss in entropy associated with the dimerization under P–P bond formation.\textsuperscript{4,5,6,7}

Detailed studies on the structural aspects of the dimerization of persistent pnictyl radicals were performed on 1 and the N-heterocyclic phosphanyl radical 3c. Comparison of the molecular geometries of 1P, 1As (as determined by gas phase electron diffraction) and their dimers \{[(Me\textsubscript{3}Si\textsubscript{2}CH)\textsubscript{2}E–E(CH–(SiMe\textsubscript{3}))\textsubscript{2}] \textsubscript{2} (1P\textsubscript{2}, E = P and 1As\textsubscript{2}, E = As) revealed that the dimerization is accompanied by bond angle distortions in the alkyl groups and a reorientation of the CH(SiMe\textsubscript{3})\textsubscript{2} substituents in a R\textsubscript{2}E unit from a syn,syn-conformation in the radicals to a syn,anti-conformation in the dimers. Backed by computational studies,\textsuperscript{6,7} these changes were interpreted as indicating that the dimers in the crystal are loaded with a substantial amount of steric strain energy. The possibility to discharge the strain upon release of the molecule from the crystal lattice was seen as a strong driving force for the formation of monomers in solution or the gas phase, and led to a description of 1 as “Jack-in-the-box molecules.”\textsuperscript{6} In a recent computational analysis\textsuperscript{8} of the dimerization of 1 it was emphasized that a realistic description of the energetics of this process requires also the consideration of dispersion forces: neglecting dispersion, the energy required for P–P bond homolysis was predicted insufficient to offset the stabilizing effect of structural relaxation in the radicals, and it is only due to the dispersive attraction between the radicals that dimer formation is energetically favoured.

A different source of energetic stabilization was discussed for the N-heterocyclic radicals 3: based on a comparison of EPR hyperfine couplings to the \textsuperscript{31}P and \textsuperscript{14}N nuclei and computational evidence, Wright et al.\textsuperscript{4d} concluded that the spin density is not mainly phosphorus-based as in other phosphanyl radicals, but rather delocalized over the heterocycle. They described these species consequently as π-radicals and postulated that their creation from the corresponding dimers should be facilitated by a combination of steric effects (repulsion between bulky substituents) and electronic stabilization by π-delocalization. In accord with this hypothesis, formation of persistent radicals 3c from dissociation of the isolable dimer \{3c\}\textsubscript{2} was observed at exceedingly mild conditions (room temperature) in solution,\textsuperscript{4c} and an experimental evaluation of the energetics of the P–P bond homolysis of the dimer \{3c\}\textsubscript{2} gave a dissociation enthalpy \(\Delta H_{\text{Diss}}\) of 79 kJ mol\textsuperscript{−1},\textsuperscript{4k} well below the average P–P bond enthalpy of 201 kJ mol\textsuperscript{−1}.\textsuperscript{3d} Computationally, the dissociation energies were greatly underestimated when dispersion forces were neglected (cf. an unrealistically low calculated dissociation energy of ≈3 kJ mol\textsuperscript{−1} for a N-Me substituted model dimer \{3d\}\textsubscript{2}),\textsuperscript{4g} and overestimated when dispersion forces were included (cf. \(\Delta H_{\text{Diss,calc}} = 95.8 \text{ kJ mol}^{-1}\) for \{3d\}\textsubscript{2} and 129.9 kJ mol\textsuperscript{−1} for \{3c\}\textsubscript{2} at the \textit{ω}B97X-D/cc-pVDZ level of theory).\textsuperscript{4k}

Summarizing the available knowledge on persistent phosphanyl (and arsanyl) radicals, it becomes clear that their common property is the stabilization against dimer formation or further reaction\textsuperscript{4k} by sterically crowded substituents. The factors controlling this stabilization have been extensively studied for a few representatives (mainly 1), but there are still many open questions which address, e.g., the interplay of steric and electronic stabilizing effects in 3 and related cyclic or open dianimophosphanyl radicals. Improving our understanding of these factors is needed in order make better use of the still underdeveloped potential of the persistent radicals in synthesis, but also to deepen our insight into the reactivity and thermal stability of E–E-bonded frameworks, and the tuning of these qualities by steric strain. Furthermore, considering that the results of computational studies seem to depend strongly on the computational model applied,\textsuperscript{4d,4k,4s} an experiment based research approach seems highly desirable in order to provide an unbiased reference point. We report here on the extension of a previous experimental study on the dissociation energetics of the diphosphan \{3c\}\textsubscript{2} to include compounds featuring both N-heterocyclic (\{4\}\textsubscript{2}, \{5\}﻿\textsubscript{2}, Scheme 2) and acyclic (\{6\}−(9)\textsubscript{2} molecular frameworks, and a discussion of the results in the light of computational studies.

**Results and discussion**

**Synthesis and characterization of sterically crowded tetraaminodiphosphanes and dianmophosphanyl radicals**

Diphosphanes \{4\}−\{6\}were prepared by reductive coupling of appropriate chlorophosphan precursor using previously published procedures.\textsuperscript{5d,10} In case of \{7\}\textsubscript{2}, the reported protocol\textsuperscript{4c} was modified by using sodium naphthalenide instead of potassium graphite as reducing agent. Finally, \{8\}\textsubscript{2} and \{9\}\textsubscript{2} were obtained analogously by reduction of the chlorophosphan precursors with magnesium or sodium (Scheme 3). Both new compounds were characterized by elemental analyses, spectral data, and single-crystal X-ray diffraction studies.\textsuperscript{†}

The individual molecules in crystalline \{8\}\textsubscript{2} (Fig. 1) display crystallographic \textit{C}_{1} symmetry and exhibit therefore a staggered conformation in which both the two R\textsubscript{2}P moieties as a whole and the two pairs of Et\textsubscript{2}N and TMP substituents are mutually \textit{trans} to each other. The nitrogen atoms adopt planar or near planar coordination geometries (sum of bond angles 360.0(4)° at N8 and 353.5(4)° at N2), and the coordination planes around these atoms are strongly twisted with respect to the

\[\text{R}^1\text{R}^2\text{PR}^3\text{R}^4 \text{⇌}\text{R}^5\text{NR}^6\text{R}^7\text{R}^8\]

\[\text{R}^1\text{R}^2\text{PR}^3\text{R}^4 \text{⇌}\text{R}^5\text{NR}^6\text{R}^7\text{R}^8\]

\[\text{R}^1\text{R}^2\text{PR}^3\text{R}^4 \text{⇌}\text{R}^5\text{NR}^6\text{R}^7\text{R}^8\]

\[\text{R}^1\text{R}^2\text{PR}^3\text{R}^4 \text{⇌}\text{R}^5\text{NR}^6\text{R}^7\text{R}^8\]

†Crystallographic data of the chlorophosphan 9,CI (the precursor of \{9\}\textsubscript{2}) are found in the ESL."
Scheme 3 Synthesis of the diphosphanes (8)2, (9)2. Reaction conditions: (i) 1 equiv. Li(tetramethylpiperidyl), THF, −78 °C to r.t.; (ii) excess Mg in THF ((8)2) or Na in hexane ((9)2), 3–7 h ultrasound at 48 °C.

Selected bond lengths [Å]: P1–N8 1.7070(16), P1–N2 1.7395(15), P1–P1#1 2.2914(10).

Table 1 P–P bond distances in strained diphosphanes

<table>
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<th>P–P [Å]</th>
<th>Ref.</th>
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</tr>
<tr>
<td>{3c}2</td>
<td>2.3204(13)</td>
</tr>
<tr>
<td>{4}2</td>
<td>2.3206(9)</td>
</tr>
<tr>
<td>{5}2</td>
<td>2.270(2)</td>
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<td>{6}2</td>
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</tr>
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<td>{8}2</td>
<td>2.291(4)</td>
</tr>
<tr>
<td>{9}2</td>
<td>2.357(2)</td>
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</table>

*The disordered crystal contains a second unit with a distance 2.3013(13) Å.

The molecules in crystalline {9}2 feature a pseudo-ecliptic alignment of the R2P units (Fig. 2) in which the P–N bonds to the TMP substituents lie nearly in one plane (dihedral angle N(2)–P(1)–P(1)’–N(2)’ 1.2(3)°) and the central NPN plane (skew angles § 62° for the TMP and 80° for the Et2N substituent). The molecules in crystalline {9}2 feature a pseudo-ecliptic alignment of the R2P units (Fig. 2) in which the P–N bonds to the TMP substituents lie nearly in one plane (dihedral angle N(2)–P(1)–P(1)’–N(2)’ 1.2(3)°) and the piperidine rings are adjacent to each other. The resulting arrangement comes close to C2v-symmetry. As in {8}2, the coordination geometry at the nitrogen atoms is quasi-planar (sum of bond angles 357.0(9)–359.2(9)°). The skew angles between the NPN unit and the iPr2N-substituent of ca. 83° are similar in {8}2 whereas the skew of the TMP ring is less pronounced (skew angles ca. 53°).

The P–P distance in {8}2 falls into the range known for other strained symmetrical diphosphanes (Table 1) whereas that in {9}2 exceeds even the longest distances reported so far (2.320–2.321 Å in {3c}2 and {4}2) by more than 3 pm. A reasonable explanation for the extreme bond lengthening may be seen in the pseudo-ecliptic conformation which is most likely enforced by the steric requirements of the substituents and maximizes the Pauli-repulsion between P–N bonds and lone-pairs at adjacent phosphorus atoms.

The 31P spectra of {8}2 display two singlets with slightly unequal intensity, and the 1H and 13C NMR spectra contain two sets of signals of Et2N and tetramethylpiperidyl (TMP) substituents. Similar features had also been observed for {7}2 and indicate the presence of a mixture of meso- and rac-diastereomers with different stereochemical configuration at the phosphorus atoms in solution. A 31P NMR spectrum of {9}2 recorded at −80 °C shows likewise two signals which coalesce, however, to a single line at higher temperature. The 1H and 13C NMR spectra display also intricate temperature dependent coalescence phenomena. In addition, a new, extremely broad resonance (Δν1/2 = 7100 Hz at r.t., cf. Fig. S3 in the ESI) grows in when the temperature is raised and reversibly disappears upon cooling. We attribute this signal to radical 9, the presence of which was independently proven by EPR spectroscopy (see below). Altogether, the observed spectral changes indicate the simultaneous occurrence of two dynamic processes, viz. reversible equilibration between {9}2 and two radicals 9 (which enables also interconversion between rac- and meso-{9}2), and freezing of the TMP ring inversion at low temperature. It should be noted that there is ample literature precedence

†Even if the electron density of the phosphorus lone-pairs is not visible in the crystal structure, the conformation of {9}2 suggests an ecliptic orientation of the lone-pairs and the P1–N12/P1′–N12′ bonds.
for the spectroscopic observation of equilibration between persistent phosphanyl radicals and their dimers,4c–d but [9]2 is to the best of our knowledge the first example where the coexistence of both reactants has been established by NMR spectroscopy.

Direct characterization of radicals was feasible by recording EPR spectra of solutions of {4}2–{9}2 in inert solvents (hexane, toluene). The signals of the radicals were readily observed at ambient (4, 9) or elevated temperature (5–8) and analysed by simulation using the EasySpin12 program (Table 2).

The spectral parameters of 4, 5 and 7 match previously published data.4e,c,f,i All signals are split into multiplets due to hyperfine coupling with the nuclear spins of the 31P (I = 1/2) and one (7–9) or two (4–6) 14N (I = 1) nuclei. In some cases, additional couplings to remote 1H or 29Si nuclei are resolved. The hyperfine couplings to phosphorus (60–84 G) are larger than in 3c [a(31P) = 42 G4g] and cover roughly the lower half of the range of couplings (63–108 G)2a in known phosphanyl radicals. The absence of resolved hyperfine coupling to one 14N nucleus in 7 had been previously noted and was attributed to the fact that couplings to nitrogen atoms in silylamino groups are usually unobservable,4a,c presumably since their steric bulk prevents a coplanar orientation of the phosphorus and nitrogen coordination planes.2a The spectra of 8, 9 reveal, however, that unequal a(14N) couplings are also observable in dialkylamino-substituted phosphanyl radicals and the absence of resolved coupling to 14N is thus not specific for silylamino groups.

Computational studies on different conformers of 6–9 confirm the expectation2c,4a that the spin density resides mainly in the phosphorus p-orbital and reveal further that its delocalization on the nitrogen atoms shows a marked conformational dependence that is largely independent of substituent type (Fig. 3 and Table 3): maximum values of the spin density, and hence the hyperfine coupling constant (a(14N) 5–6 G), are found when the coordination planes at the phosphorus and nitrogen atoms are coplanar, and minimum values (|a(14N)| < 1 G) when they are close to perpendicular.

Based on this correlation, we can confirm the association of the large hyperfine coupling in 7 with the NiPr2 group5a,c and conclude further that the splittings in the spectra of 8, 9 arise from interaction with the NR2 (R = Et, iPr) groups and the coupling to the TMP substituent is unresolved. The observation that a(14N) in 4–6 is smaller than in 7–9 (Table 2) may be attributable to the presence of librational motion of the R2N-groups in the real molecules which cannot be reproduced computationally. However, the calculations support the earlier conjecture4e that the reduction of a(31P) and simultaneous increase of a(14N) in 3c coincides with extended delocalization of the spin density over the complete ring (Fig. 3).

**Thermochemistry of phosphane dissociation**

Thermochemical parameters for the dissociation of the phosphanes according to R2P−PR2 ⇄ 2 R3P′ may be derived from the temperature dependent variation of the equilibrium constants.
The translational contribution to the reaction entropy is identical in all cases, this change implies that the loss of internal conformational flexibility associated with radical dimerization must increase significantly from 5 over to 4c. Without going into detail, we presume that the difference between the last two species owes to the rigidity of the unsaturated heterocyclic ring in 3c, which severely reduces the conformational freedom of the N-aryl groups. The further shift of the dissociation equilibrium to the side of the dimer in case of 5c is exclusively attributable to the change in $\Delta S_{\text{Diss}}$ and may be qualitatively explained by assuming that the restrictions in the conformational freedom upon dimerization decrease with the number of bulky $\sigma$-alkyl substituents in the N-aryl moieties.

A summary of the thermochemical parameters derived from these measurements is given in Table 4, and a detailed account is contained in the ESL.†

Evaluation of the data in Table 4 reveals that although the radicals 4–9 are spectroscopically readily observable as persistent species at ambient or elevated temperature, the dissociation equilibria lie in all cases but 9c extensively on the side of the diphosphane, and the dissociation affects generally far less than 1% of the dimers even at temperatures as high as 120 °C. In case of 9c, the calculated degree of dissociation for a solution of 1 mmol initial concentration of 0.65(5) at 295 K clearly exceeds the value of 0.063(7) for 3c, and attests that radicals predominate under these conditions.

The observation of a large variability in $\Delta H_{\text{Diss}}$ and $\Delta S_{\text{Diss}}$ reveals, however, that structural changes have nonetheless a significant impact on the energetics of the bond fission. Comparing the dissociation energetics of 4c and 5c with that of 3c2 shows that introduction of the CC double bond goes along with a decrease in $\Delta H_{\text{Diss}}$ by some 23–25 kJ mol$^{-1}$. In view of the presence of identical or at least similar substituents in all species, attractive dispersion forces between the two R,P fragments in the dimers are not expected to change greatly, and the lower dissociation enthalpy for 4c is thus considered to reflect mainly the postulated extra stabilization of radical 3c by $\pi$-delocalization effects.

It should be noted, however, that the exceptional dissociation tendency of 3c2 (as evidenced by the drastic decrease of $\Delta G_{\text{Diss}}^{295}$ as compared to 4c and 5c) is not attributable to the enthalpy lowering alone, but is assisted by a simultaneously large increase in the entropic term. Since the

<table>
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<th>Diphosphane</th>
<th>$\Delta G_{\text{Diss}}^{295}$ [kJ mol$^{-1}$]</th>
<th>$pK_{\text{Diss}}$ a</th>
<th>$\Delta H_{\text{Diss}}$ [kJ mol$^{-1}$]</th>
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a $pK_{\text{Diss}} = -\log(K_{\text{Diss}}(295 K)/[\text{mol} l^{-1}])$. b Data from ref. 4c.
cicular geometries of dimers and radicals were first energy optimized using the solid-state structures as starting points, and the nature of the final geometries as local minima on the energy hypersurface was then validated by frequency calculations. In case of the radicals 7–9 and the diphosphanes {4}2, {6}2, and {8}2, we located alternative conformers that were likewise local minima on the energy hypersurface but proved energetically less stable (wise local minima on the energy hypersurface but proved energetically less stable (Fig. 4) reveals a reasonable match for torsion radical fragments to their equilibrium geometry, of the preparation energy13 of the dissociation reaction R2P–PR2 ↔ 2R2P (R2P = 3c, 4–9) computed at the ωB97x-D/cc-pVDZ level of theory.

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<th>ΔE_{frag}</th>
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* ΔPb = contribution from empirical dispersion terms. *b Data from ref. 4k.

Table 5: Bond distances (P–P in Å) and energy data (all quantities in kJ mol⁻¹) for the dissociation reaction R2P–PR2 ↔ 2R2P (R2P = 3c, 4–9) computed at the ωB97x-D/cc-pVDZ level of theory.

Fig. 4: Top: Plot of calculated energies (ΔE_{zpe} including zero-point vibrational correction, red squares) and enthalpies of dissociation (ΔH_{298}, blue diamonds) vs. experimental values of ΔH_{Diss, exp}. Bottom: Plot of calculated free energies of dissociation (ΔG_{298}) vs. experimental values of ΔG_{Diss}. Open and filled symbols refer to N-aryl (3c)2–(5)2 and N-allyl/silyl derivatives (6)2–(9)2, respectively. Red and blue trend lines were determined from linear regression analysis (the red square in the lower plot refers to (6)2 and is considered an outlier), and the dotted grey line denotes the relation ΔG_{298} = ΔH_{Diss}.

A similar deviation between calculated bond enthalpies/energies of N-allyl/silyl- and N-aryl-substituted diphosphanes was also found at the M06-2X/cc-pVDZ level.
The results of the energy decomposition analysis listed in Table 5 indicate that the variations in $\Delta E_{\text{frag}}$ are not only much smaller than those of the total energy term ($\Delta E_{\text{zpe}}$ or $\Delta H^{298}$), but show also a different response to structural changes. With the exception of $\{3c\}_2$ (where a contribution from electronic stabilization by $\pi$-delocalization must be taken into account), $\Delta E_{\text{frag}}$ in both N-heterocyclic and acyclic compounds dwindles with increasing steric demand of the substituents, which suggests that its variation reflects mainly the bond weakening or strengthening associated with the modulation of repulsive interactions between bulky peripheral groups. Given that the P–P bond lengthening in sterically congested diphosphanes is commonly ascribed to the same origin,\textsuperscript{8} it is not surprising with 20\textsuperscript{80.5 kJ mol$^{-1}$} to dissociation energies between di\textsuperscript{80% of the magnitude of $\Delta E_{\text{frag}}$} or experimentally determined enthalpies $\Delta H_{\text{Diss}}$ – correlate with the variation in P–P distances (Fig. 5). Even if a clear-cut partitioning between ‘intrinsically’ bond energy and strain energy in congested molecules is not a trivial task,\textsuperscript{7} we conclude that $\Delta E_{\text{frag}}$ can serve as an – at least approximate – measure of P–P bond strength. Since the values of $\Delta E_{\text{frag}}$ come close to the average P–P bond enthalpy\textsuperscript{9} of 201 kJ mol$^{-1}$ and approach the dissociation energy of sterically uncongested diphosphanes (239–368 kJ mol$^{-1}$ for R–R, R–PR, R–P–PR, with $R = H, Et, F, Cl, I$\textsuperscript{16}), the P–P bonds in $\{3c\}_2$–$\{9\}_2$ cannot be considered as intrinsically particularly weak. It must be conceded, however, that as in case of $\{1\}_8$, attractive dispersion forces (epitomized by the empirical dispersion term $E^{D}$) make a considerable contribution to the total adhesion energy. This contribution is clearly dominant for $\{3c\}_2$, and $\{4\}_2$ where it represents 70–80% of the fragmentation energy.

The relaxation energies $\Delta E_{\text{relax}}$ which stabilize the radicals $\{3c\}_2$ through structural adaptation and conformation changes are, like in $\{1\}_8$, smaller than the fragmentation energies, but with 20–60% of the magnitude of $\Delta E_{\text{frag}}$ still substantial. Furthermore, the variation between different radicals ($\Delta \Delta E_{\text{relax}} = 80.5$ kJ mol$^{-1}$) is twice as large as that of the fragmentation energies ($\Delta \Delta E_{\text{frag}} = 41.0$ kJ mol$^{-1}$) and must thus be seen as the dominant energetic contribution in explaining the trend in dissociation energies between different diphosphanes. Structural relaxation of the acyclic radicals $\{6\}_9$ provides generally a larger energy release ($\Delta E_{\text{relax}}$ 80–122 kJ mol$^{-1}$) than relaxation of the N-heterocyclic species $\{3c\}_2$ ($\Delta E_{\text{relax}}$ 41–60 kJ mol$^{-1}$) and is associated with additional conformational changes (Fig. S12 in the ESI†). These findings support at first glance the perception of the dimers $\{6\}_9$–$\{9\}_2$ as sterically strained “jack-in-the-box” molecules which can release their strain energy by undergoing geometrical and conformational adaptation during dissociation. However, we must also consider that the variation in skew angles or the pyramidalization of NR groups associated with a conformational change may affect the spin density delocalization, and thus the electronic stability, of the radicals. In order to assess the importance of these effects, we analysed the conformational preferences of the parent diaminophosphanyl radical ($H_2N$)$_2$P+ ($\{10\}_4$) and the appropriate cation ([($H_2N$)$_2$P]$^+$ ($\{10\}_4$), assuming that the impact of steric constraints is in these species negligible and any changes will be dominated by electronic effects. Geometry optimizations were carried out using DFT (B3LYP with (aug)-cc-pVDZ and aug-cc-pVTZ basis sets) and coupled cluster (CCSD/aug-cc-pvdz) methods. The results did not differ significantly, and we will only discuss those of the CCSD calculations (Fig. 6).

The cation $\{10\}_4$ exhibits, as expected, a $C_{2v}$-symmetrical planar geometry with rather short PN distances of 1.643 Å. Geometry optimization of a conformer obtained by rotation of one NH$_2$ group by 90° led to the localization of a transition state 17.8 kJ mol$^{-1}$ higher in energy than the ground state. The ‘orthogonal’ amino substituent is characterized by a lengthened PN bond (1.715 vs. 1.632 Å for the ‘in plane’ NH$_2$ group) and a slightly pyramidal geometry at the N-atom. The computational results are in accord with the established view of aminophosphonium ions\textsuperscript{17,18} as delocalized, allyl-anion analogue $\pi$-systems in which rotation of NR$_2$ groups (which parallel disrupts the $\pi$-delocalization) is impeded by a significant energy barrier. In contrast, radical $\{10\}_4$ features a non-planar, $C_{2v}$-symmetrical ground state geometry with twisted orientation of the NH$_2$ groups (skew angle 30°), pyramidal coordination at the N-atoms (sum of bond angles 343°) and lengthened PN bonds (1.752 Å). The search for a rotational transition state yielded a $C_{2v}$-symmetrical geometry in which the average PN distance remains essentially unchanged (PN 1.773, 1.737 Å, 0.89).

**Fig. 5** Plot of computed fragmentation energies $\Delta E_{\text{frag}}$ vs. bond distances. The straight line is the result of a linear regression analysis ($R^2 = 0.89$).

**Fig. 6** Computed molecular structures and relative energies (in kJ mol$^{-1}$) at the CCSD/aug-cc-pVDZ level of theory for the electronic ground states (left) and rotational transition states (right) of $\{10\}_4$ and $\{10\}_4$.
average 1.755 Å) and the pyramidalization in the ‘orthogonal’ NH₂ group increases further (sum of bond angles at N 331°). The transition state energy lies by merely 2.0 kJ mol⁻¹ above that of the ground state, indicating that the energetic barrier to NH₂-group rotation is negligible and the geometrical changes associated with this process do not affect radical stability. This pronounced difference to the cation is easily rationalized if one considers that placement of an extra electron in the (PN-antibonding) LUMO of the cation reduces the π-bond order, and thus the available stabilization from π-delocalization. Consequently, the remaining interaction between an unpaired electron on the P-atom and the nitrogen lone-pairs in aminophosphanyl radicals should be better described as hyperconjugative, and its tuning by rotational reorientation of NH₂ (or NR₂) groups offers – unlike as in aminophosphonium ions¹⁷ – only minor opportunities for electronic (de)stabilization.

The computational studies on 10⁺ and 10⁻ imply that the orientational reorganization of phosphorus π-orbitals and nitrogen lone-pairs which arises from embedding of an NPN into a five-membered heterocycle¹⁸,¹⁹ offers an energetic advantage for aminophosphonium cations, but not for radicals, and that the NPN unit of the latter provides, apart from possible constraints imposed by a cyclic molecular structure, no further restoring force to maintain local planarity. We are thus prompted to conclude that the structural reorganization of the radicals formed during dissociation of tetraamino-diphosphanes is not associated with any extra electronic stabilization of the unpaired electron, but is essentially driven by steric factors. In turn, the inhibition of structural relaxation by a geometrical constraining cyclic structure must be considered to have an adverse effect on dissociation enthalpies, which helps to explain why P-P bond fission is slightly more endothermic for the heterocyclic dimers {3c}₂⁻{5}² than for {7}²⁻{9}².

Conclusions

Thermochemical data for the homolytic P-P bond fission of a series of sterically congested diphosphanes (two of which were newly synthesized and fully characterized) were determined. The values of free reaction energies ΔG²⁹₅_{diss} and pK²⁹₅_{diss} indicate that the dissociation affects in most cases only a small fraction of the diphosphanes, and the concentration of persistent radicals – even if they may be spectroscopically observable at ambient temperature – remains small. A notable exception is {9}², where the degree of dissociation (for a 1 mM solution at 295 K) is by an order of magnitude larger than for the N-heterocyclic diphosphane {3c}₂. The acyclic radical 9 must thus be considered as even more stable than 3c which benefits from electronic stabilization by π-delocalization.⁶⁹

Analysis of trends in experimental data in connection with computational studies allowed us to relate the variations in ΔG²⁹₅_{diss}/pK²⁹₅_{diss} to both enthalpy and entropy effects. Stabilization of radicals relative to dimers with a concomitant decrease in dissociation enthalpies ΔH²⁹₅_{diss} is mainly due to structural relaxation (adaptation of bond angles and – for the acyclic species 6–9 – conformational changes) and driven by the need to minimize steric congestion. Electronic stabilization by P,N-π-conjugation, which is crucial for amino-phosphonium cations,¹⁷,¹⁸ is hardly of importance for aminophosphoryl radicals, and the energetic effect of cyclic π-delocalization in 3c is visible but stands back. The radical stabilizing influences are offset by strong attractive dispersion forces, which are once more⁸ stated that the monomer – dimer equilibrium is predominantly governed by the balance of attractive dispersion forces and entropic factors. However, the results presented here emphasize that the different aspects of structural relaxation (in particular the conformational changes enabling “Jack-in-the-box” behaviour⁴) are also vital for the explanation of the trends in dissociation enthalpies and entropies between different molecules. Furthermore, it appears that computational models tend to overestimate the entropy term associated with the diphosphate dissociation, and yield thus free reaction energies which are systematically too low.

Experimental

Materials and methods

All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra were recorded on Bruker Avance AV 400 or AV 250 instruments (¹H: 400.1/250.0 MHz, ¹³C: 100.5/62.9 MHz, ³¹P: 161.9/101.2 MHz); chemical shifts were referenced to ext. TMS (¹H, ¹³C), 85% H₃PO₄ (δ = 40.480747 MHz, ³¹P). Elemental analyses were carried out using an Elemental Micro Cube. Melting Points were determined with a Büchi B-545 melting point apparatus in sealed capillaries. EPR spectra were measured with a Bruker EMX X-band spectrometer. Hyperfine splittings were determined by spectral simulation with the program EasySpin.¹² Quantitative EPR measurements and evaluation of thermochemical data from the spectral data were carried out using the same protocol that had been applied in case of {3c}₂. A detailed description has been given elsewhere.⁴⁸

Chlorophosphane precursors (iPr₂NP)Cl₂,¹⁹ (Me₃Si)₆N(iPr₂N)PCl₄,⁴⁴ (iPr₂N)₆N(iPr₂N)PCl₄ and (TMP)(iPr₂N)PCl₂¹¹ and the diphosphanes {4}⁹,⁰ {5}⁴,⁲ and {6}²,¹⁰ were prepared as described elsewhere. Diphosphane {7}₂ was prepared by a modification
of the reported procedure, using sodium naphthalene instead of potassium graphite as reducing agent.

**Synthetic procedures**

Chloro(diethylamino)(2,2,6,6-tetramethylpiperidyl)phosphine 8 Cl. nBuLi (4.5 mL of a 2.3 M solution in hexane, 10.50 mmol) was added dropwise at −78 °C to a solution of 2,2,6,6-tetramethylpiperidine (1.80 mL, 10.50 mmol) in THF (10 mL). The mixture was then allowed to warm to room temperature and stirred for 30 min. This solution was then added dropwise to a cooled (−78 °C) solution of Et3NPc1 (1.83 g, 10.50 mmol) in THF (15 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were then removed under reduced pressure. The residue was extracted with 15 mL hexane and filtered. The filtrate was evaporated to dryness and the resulting orange oil used without further purification.

Volatiles were then removed under reduced pressure. The resulting orange oil used without further purification. The mixture was heated for 3 h to 48 °C in an ultrasound bath. Yield 0.50 g (25%).

1,2-Bis(diethylamino)-1,2-bis(2,2,6,6-tetramethylpiperidyl)-diphosphane {8}2. Mg chips (excess) and a crystal of I2 were added to a solution of 8 Cl (1.21 g, 4.1 mmol) in THF (10 mL). The mixture was heated for 3 h to 48 °C in an ultrasonic bath. The solvent was then removed under reduced pressure and the residue extracted with 10 mL of hexane and filtered. The filtrate was stored at −24 °C until a crystalline product formed. Yield 0.50 g (25%). - M.p. 98 °C. - 31P{1H} NMR (C6D6): δ = 99.2, 91.6 (s). Isomer 1 α: 1H NMR (C6D6): δ = 3.35 (m, 8 H, CH2CH2), 1.72–1.67 (m, 12 H, CH2CH2CH2); 1.40 (br s, 24 H, CH3), 1.11 (t, JHH = 7.2 Hz, CH3CH2). Isomer 2: 1H NMR (C6D6): δ = 3.40 (m, 8 H, CH2CH2), 1.67–1.63 (m, 12 H, CH2CH2CH2); 1.52 (s, 12 H, CH3), 1.49 (s, 12 H, CH3), 1.13 (t, JHH = 7.3 Hz, CH3CH2). - 13C{1H} NMR (C6D6): δ = 45.5 (br s, CH3), 38.4–27.5 (br m, CH3), 31.6 (br s, CH3), 13.8 (br s, CH3). Quaternary carbon atoms could not be detected because of the low signal-to-noise ratio. −C26H56N4P2, (M = 486.69 g mol−1); calc C 66.38 H 11.88 N 10.32; found C 64.16 H 11.60 N 11.51.

Crystal structure determinations

Diffraction studies were carried out using a Bruker diffractometer equipped with a Kappa APEX II Duo CCD-detector and a KRYO-FLEX cooling device with Mo-Kα radiation (λ = 0.71073 Å) at T = 100 K. The structures were solved by direct methods (SHELXS-9722) and refined with a full-matrix least-squares scheme on F2 (SHELXL-201422). Semi-empirical absorption corrections were applied for all structures. Non-hydrogen atoms were refined anisotropically, and H atoms with a riding model, on . Details of the crystal structure determinations are listed in Table 6. For {9}2, the absolute structure parameter22 was refined as x = 0.00(10). Details of the crystal structure determinations are listed in Table 6 (for 9 Cl in the ESI†).

<table>
<thead>
<tr>
<th>Table 6 Crystallographic data for {8}2 and {9}2</th>
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<td>Abs. coeff. μ (mm−1)</td>
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Data collected | 19704 | 20756 |
Unique data | 2901 | 5756 |
Observed data with I > 2σ(I) | 2248 | 3419 |
Restraints | 0 | 0 |
Variables | 145 | 325 |
R1(I > 2σ(l)) | 0.041 | 0.066 |
wR2 | 0.108 | 0.113 |
GOF | 1.034 | 0.992 |
Max. diff. dens. (e Å−3) | 0.483 | 0.329 |
Min. diff. dens. (e Å−3) | −0.302 | −0.313 |
Computational studies

Computational studies were performed with the Gaussian09 suite of programs. Computations on \(4-9\) and \(\{4\}_2-\{9\}_2\) were carried out using the \(\omega\)B97X-D functional by Head-Gordon with cc-pVDZ basis sets. Explorative calculations were also carried out with Troullar's M06-2X functional and the same basis. Attempts to use larger basis sets (i.e. including diffuse functions or of triple zeta quality) failed due to numerical or computation time problems. Numerical integrations were performed on an ultrafine grid. Since an attempt to model the dissociation of \(6\) in solution showed that inclusion of solvent effects by a PCM model had no significant effect (\(\Delta E_{\text{XPE}} < 3 \text{ kJ mol}^{-1}\) for the reaction and \(\Delta E_{\text{ZPE}} < 3.3 \text{ kJ mol}^{-1}\) for individual reactants), we further resorted from using a solvation model. Molecular structures were first energy optimized without symmetry constraints using the XRD data as starting points. Harmonic frequencies and zero-point energies (ZPE) at optimized gas phase structures were calculated at the same levels and showed all molecular geometries to present local minima (only positive eigenvalues of the Hessian matrix) on the potential energy surface. Energies (including vibrational zero-point correction), enthalpies, and free enthalpies calculated for the dissociation reactions are corrected for basis set superposition error (BSSE), the necessary corrections being obtained by counterpoise calculations. Computations on \(10^{-10}'\) were carried out with the B3LYP/(aug)-cc-pVDZ and CCSD/(aug)-cc-pVDZ levels; both approaches gave similar results, and only the CCSD results will be discussed. MOLDEN and GABEDIT were used for visualization, and NPA spin densities were computed with the program AOMIX.

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Notes and references


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