peri-Interactions in Naphthalenes, 3 [1].
On Hypercoordination in 8-Dimethylamino-naphth-1-yl-phosphonium salts and -phosphines

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Naphthalenes. 1H NMR Data, 31P NMR Data, Interatomic Distances, Repulsive Interaction
In (alkyl)(aryl)(8-dimethylamino-naphth-1-yl)phosphonium salts and in the parent phosphines, there is no experimental evidence of dative N—P interactions. Conclusions to the contrary are based on the choice of improper standards of comparison.

Introduction

peri-Disubstituted naphthalenes continue to be cherished objects of research for the investigation of donor/acceptor (D—A) interactions. This includes compounds with donor substituents D of only moderate nucleophilicity and “acceptor” substituents A whose electrophilicity is, at best, rather weak or even doubtful. E. g., a peri-dimethylamino group or even a methoxy group has frequently been chosen as the donor substituent [2], though 1-dimethylamino-naphthalene and 1-methoxy-naphthalene are of the dimethylaniline and anisole type, respectively.

Among tertiary amines, dimethylaniline is a fairly weak nucleophile. In 8-substituted 1-dimethylamino-naphthalenes, sterical hindrance in the peri space forces the (CH3)2N group out of the C10 plane (see formula 1) [3] so that efficient resonance of the lone pair at N and the aromatic system is precluded; however, the N atom, bound to two sp3-carbons and one sp2-carbon atom, nevertheless is a much poorer nucleophile than in aliphatic tertiary amines (for comparison – mutatis mutandis – note that 1-dimethylamino-naphthalene is less basic and N,N,2,6-tetramethyl-aniline (2) only very slightly more basic than dimethylaniline whereas all three of them are less basic than trimethylamine by more than five powers of ten in the Kb scale [4]). In 1-methoxy-naphthalenes, sterical inhibition of resonance is much smaller even in the presence of 8-substituents, and the σ-donicity of the anisole-type oxygen atom is, indeed, very poor.

Among the “acceptor” substituents, amide [2], silyl [5] and phosphino groups [6 - 9] have been used which range, at best, at the bottom end of any electrophilicity scale. Such choice is surprising because the geometry of the fairly rigid naphthalene skeleton puts the peri substituents at a “natural” distance of ca. 250 pm [10, 11], much too long for a conventional bonding interaction [12]. The formation of a dative bond D—A [13] of normal length would require a considerable distortion of the C10 skeleton whose energetic bill could be paid only by a strong peri bond (such as a C-C or an amide N-CO bond [14]). For the bonding interaction between a weak nucleophile and a poor electrophile, the naphthalene skeleton would act as a spacer which prevents the substrates from coming into bonding distance.

Though still very moderately so, a phosphonium phosphorus atom is a better electrophile than P in phosphines [15]. Earlier, we had investigated the possibility of a dative (CH3)2N—P+ interaction in (alkyl)(8-dimethylamino-naphth-1-yl)-[=DAN]di(phenyl)phosphonium salts [16]. Such interaction could be described either as an isomerism (3A = 3B) or as a bond/no bond resonance (3A → 3B) [16]. In the former case, the properties of the respective compounds should reveal which isomer is the favoured one. In the latter case, within a qualitative application of the VB formalism, the bond

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and the no bond formulae may enter a VB treatment with coefficients so different that the actual compound may adequately be described by only one formula, and the contribution of the other one may be neglected. Since the consequences are the same, it suffices to find out which formula describes best the actual properties of the respective cations.

By $^1$H NMR methods, we had previously established that in the phosphonium cations 3a - c, the P atom (rather than the N atom) is the centre of positive charge [16]. From this experimental fact, we had concluded that formula 3A is a perfectly adequate representation of the cations, and that there is no indication that formula 3B plays any significant role, i.e. that in these cations, the phosphorus is not hypercoordinate. $^{31}$P NMR was in accord with these conclusions inasmuch as $\delta(P^+-C//3) = 3.00$ ppm (in CD$_2$C$_2$I$_2$) [18] and Hendrickson’s $\delta(P^+-C//3)(4aI) = 3.12$ ppm (in CDCl$_3$) [19]. In fact, minute as it is, this $\Delta\delta$ does not reflect an N→P$^+$ dative bond in 3ai but a solvent effect, since in CDCl$_3$, we had found $\delta(P^+-C//3)(3aI) = 3.13$ ppm [20], virtually identical with $\delta = 3.12$ ppm in 4ai considering the precision of the instruments (90/60 MHz [19-21]). For the ethoxycarbonylmethyl phosphonium bromide 3dII, a somewhat larger highfield shift ($\Delta\delta = -0.75$ ppm) has been inferred from $\delta(P^+-C//H_2)(3dII) = 4.95$ ppm (250 MHz, CDCl$_3$) [8] and Hendrickson’s $\delta(P^+-C//H_2) = 5.7$ (60 MHz, CDCl$_3$) of (methoxycarbonylmethyl)tri(phenyl)phosphonium chloride [19, 22]. However, it is well known that in CDCl$_3$ (and CD$_2$C$_2$I$_2$), due to the formation of contact ion pairs, P$^+$-C-H protons in phosphonium chlorides absorb at slightly lower field than in the bromides [23] so that part of this $\Delta\delta$ has to be assigned to a CIS effect [24]. Furthermore, in CD$_2$C$_2$I$_2$, the ethyl ester 4bII ($\delta = 5.37$ ppm [25]) absorbed

Results and Discussion

For 3ai, Corriu’s conclusion is based on a “highfield shift” of $\Delta\delta(P^+-C//H_3) = -0.12$ ppm, with respect to 4ai. This $\Delta\delta$ was obtained from our $\delta(P^+-C//H_3)(3ai) = 3.00$ (in CD$_2$C$_2$I$_2$) [18] and Hendrickson’s $\delta(P^+-C//H_3)(4ai) = 3.12$ ppm (in CDCl$_3$) [19]. In fact, minute as it is, this $\Delta\delta$ does not reflect an N→P$^+$ dative bond in 3ai but a solvent effect, since in CDCl$_3$, we had found $\delta(P^+-C//H_3)(3ai) = 3.13$ ppm [20], virtually identical with $\delta = 3.12$ ppm in 4ai considering the precision of the instruments (90/60 MHz [19-21]). For the ethoxycarbonylmethyl phosphonium bromide 3dII, a somewhat larger highfield shift ($\Delta\delta = -0.75$ ppm) has been inferred from $\delta(P^+-C//H_2)(3dII) = 4.95$ ppm (250 MHz, CDCl$_3$) [8] and Hendrickson’s $\delta(P^+-C//H_2) = 5.7$ (60 MHz, CDCl$_3$) of (methoxycarbonylmethyl)tri(phenyl)phosphonium chloride [19, 22]. However, it is well known that in CDCl$_3$ (and CD$_2$C$_2$I$_2$), due to the formation of contact ion pairs, P$^+$-C-H protons in phosphonium chlorides absorb at slightly lower field than in the bromides [23] so that part of this $\Delta\delta$ has to be assigned to a CIS effect [24]. Furthermore, in CD$_2$C$_2$I$_2$, the ethyl ester 4bII ($\delta = 5.37$ ppm [25]) absorbed
Table 1. NMR data of the phosphonium salts Ar(C₆H₅)₂P+-CH₂-R X-.

<table>
<thead>
<tr>
<th>Nr.²</th>
<th>Ar</th>
<th>R</th>
<th>X</th>
<th>Solvent</th>
<th>¹H NMR: δ [ppm]</th>
<th>¹³C NMR: δ [ppm]</th>
<th>³¹P NMR: P⁺ [ppm]</th>
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<tr>
<td>4aI</td>
<td>C₆H₆</td>
<td>H</td>
<td>I</td>
<td>CDCl₃</td>
<td>3.17</td>
<td>d, 13.2</td>
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<tr>
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<td>H</td>
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<td>3.27</td>
<td>d, 12.8</td>
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<td>H</td>
<td>I</td>
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<td>3.19</td>
<td>d, 12.8</td>
<td>+23.36</td>
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<tr>
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<td>H</td>
<td>I</td>
<td>CDCl₃</td>
<td>3.21</td>
<td>c, dd, 13.0</td>
<td>+29.51</td>
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<tr>
<td>iso-4d</td>
<td>2-F-C₆H₅H(1)</td>
<td>H</td>
<td>B(C₆H₅)₃</td>
<td>CD₂Cl₂</td>
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<td>H</td>
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<td>B(C₆H₅)₃</td>
<td>CD₂Cl₂</td>
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<td></td>
<td>COOC₂H₅</td>
<td>Br</td>
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<td>d, 13.8</td>
<td>+21.40</td>
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<tr>
<td>4fII</td>
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<td></td>
<td>COOC₂H₅</td>
<td>Br</td>
<td>5.47</td>
<td>d, 13.6</td>
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<tr>
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<td>C₆H₆H(1)</td>
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<td>H</td>
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<td>CD₂Cl₂</td>
<td>4.61</td>
<td>l, 14.2</td>
<td>+22.13</td>
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</table>

² References attached to the compound numbers refer to the method of synthesis: b (CH₃)₂N: s, δ 2.08; c C₆H₅OH: O-CH₂: q, δ 3.70. J(¹H,¹H) = 7.0 Hz; c C₆H₅: t, δ 1.22. J(¹H,¹H) = 7.0 Hz; d J(¹H,¹⁹F) = 3.7 Hz; e d, J(³¹P,¹⁹F) = 15.3 Hz; ³¹P NMR (188.31 MHz; ref.: CFC₁₃); f d, J(³¹P,¹⁹F) = 3.4 Hz. ³¹P NMR (188.31 MHz; in CDCl₃; ref.: CFC₁₃); g, δ -90.08, J(¹⁹F,³¹P) = 3.5 Hz; h O-CH₂: q, δ 4.04, J(¹H,¹⁹F) = 7.1 Hz; i H-C₆H₅: t, δ 1.05, J(¹H,¹⁹F) = 7.1 Hz; j O-CH₂: q, δ 3.82, J(¹H,¹⁹F) = 7.1 Hz; k C-CH₂: t, δ 0.76, J(¹H,¹⁹F) = 7.1 Hz; l (CH₃)₂N: br, s, δ 1.96. ³¹P NMR: P⁺. ³¹P NMR: P⁺.

by δδ = -0.16 ppm at higher field than the corresponding methyl ester (δ = 5.53 ppm [26]). The ³¹P NMR absorption of 3dII, δ = +22.6 ppm [8], is perfectly within the (alkyl)tris(aryl)phosphonium range [27]. In our opinion, therefore, the published data are not indicative “of N-P intramolecular dative interactions” [8]. On the other hand, we are not aware of arguments which invalidate our previous conclusions to the contrary [16].

For a more subtle study of the situation, we looked at 8-unsubstituted and other 8-substituted (napth-1-yl)phosphonium salts 4c - g. Since most of the earlier NMR data had been obtained on low precision equipment, new spectra were recorded under standardized conditions (¹H-NMR: 200.13 MHz, ³¹P-NMR: 81.015 MHz, solvent: CDCl₃ whenever possible). The data are collected in Table 1.

Ar(C₆H₅)₂P⁺-CH₂-R X⁻ (4).

- 4a: R = H, Ar = C₆H₆;
- 4b: R = COOC₂H₅, Ar = C₆H₆;
- 4c: R = H, Ar = C₁₀H₁₁(1);
- 4d: R = H, Ar = 8-F-C₁₀H₁₁(1);
- 4e: R = H, Ar = 8-I-C₁₀H₁₁(1);
- 4f: R = COOC₂H₅, Ar = C₁₀H₁₁(1);
- 4g: R = C₆H₅; Ar = C₁₀H₁₁(1).

¹H NMR, δ(P⁺-CH₂-R)

In the series of methyl phosphonium salts (R = H), replacement of one phenyl in 4aI by a (napth-1-yI) group causes a downfield shift of δ(4cI/4aI) = +0.10 ppm. Upon introduction of a (CH₃)₂N group into its 8-position, this minute shift is cancelled so that 3aI and 4aI absorb at virtually the same field (formally 3aI at lower field by δ(3aI/4aI) = +0.02 ppm) so that the purported "highfield shift" is, in fact, non-existent. 8-F behaves very similar (δ(4dI/4cI) = -0.06 ppm); δ(P⁺-CH₃) of 4dI must, however, be treated with caution: As borne out by the elemental analysis and the ¹H NMR spectrum, the salt crystallized as an ethanol-solvate. In CDCl₃ solution, this ethanol may specifically solvate the cation or the anion and thus significantly alter the microenvironment of the P⁺-CH₃ protons, with consequences for the signal position. 8-I causes a further downfield shift of δ(4eI/4cI) = +0.20 ppm (δ(4eI/4aI) = +0.30 ppm). In view of the small shifts, we restrict ourselves to the trivial conclusion that substituents in the close vicinity of the P⁺-methyl groups naturally have a certain influence upon their δ(P⁺-CH₃).
ment of one phenyl by a (naphth-1-yl) group has almost no effect ($\Delta \delta(4\text{II}/4\text{III}) = +0.07$ ppm). Introduction of (CH$_3$)$_2$N into the 8-position causes a highfield shift of $\Delta \delta(3\text{II}/4\text{II}) = -0.57$ ppm. For the corresponding benzyli-phosphonium bromides ($R = C_6H_5$), we had to turn to methanol as solvent because of insufficient solubility of (benzyl)-(naphth-1-yl)diphenyl) phosphonium bromide in CDC$_3$ (and CD$_2$Cl$_2$). Introduction of an 8-(CH$_3$)$_2$N group into 4gII causes a highfield shift of the CH$_2$ signal by $\Delta \delta(3\text{II}/4\text{II}) = -0.59$ ppm, almost identical with $\Delta \delta(3\text{II}/4\text{II})$.

Though certainly significant, these signal shifts do not provide evidence for dative N$\rightarrow$P$^+$ bonding, since other explanations are at hand and can, as far as we can see, not be ruled out: First, as in the P$^+$$\rightarrow$CH$_3$ series, any change in the vicinity of the P$^+$$\rightarrow$C$^-$H protons must to some extent be reflected by the $^1$H NMR signal position. Second, in the peri space, there is considerable sterical hindrance. In 1-dimethylamino-naphthalene, the N$-$CH$_3$ signal ($\delta = 2.91$ ppm [28]) is shifted to higher field by $\Delta \delta = -0.16$ ppm upon introduction of a peri-bromine [29]. We found such highfield shifts to be a general phenomenon for peri-substituted 1-dimethylamino-naphthalenes [30]; it is easily rationalized by a change of the rotamer equilibrium due to sterical hindrance, viz. a decrease of the population of the rotamer having the (CH$_3$)$_2$N group coplanar with the naphthalene skeleton (see formula 1) [31]. A similar effect of peri-substituents in (naphth-1-yl)phosphonium salts upon the rotamer equilibrium originating from rotation around the C$_{\text{naphth-1-yl}}$-P$^+$ bond might influence $\delta(\text{P}^+\rightarrow\text{CH}_2\rightarrow\text{R})(\text{R} = \text{H}, \text{COOC}_2\text{H}_5$, C$_6\text{H}_5$). This effect may be stronger in 4f,g than in 4c because of increased sterical hindrance, and it may be enhanced by a similar effect at the C$_{\text{methylene}}$-C$_R$ bond by which the averaged positions of the methylene protons with respect to the anisotropy cone of the C=O group of the C$_n$ plane are changed [32]. Such rationalizations are only tentative but preclude a decision in favour of N$\rightarrow$P bonding.

$^{31}$P NMR, $\delta(\text{P}^+)$

The $^{31}$P nucleus in (alkyl)tri(aryl)phosphonium salts absorbs within a fairly narrow range, in most cases between $\delta = ca. +20$ and +25 ppm [33]. Formula 3B would represent an (alkyl)(ammonio)tri(aryl)phosphorane. Authentic structures of this class of compounds are not known but would be expected to absorb at much higher field. According to this criterion, the (DAN)phosphonium salts are in full accord with the P-octet formula 3A (see Table 1). The peri-F salt 4eI ($\delta(\text{I}^{31}\text{P}) = +25.72$ ppm) absorbs at slightly lower field, but still within the tetraorganophosphonium range. In the peri-F salt 4dI ($\delta(\text{I}^{31}\text{P}) = +29.51$ ppm), a modest shift to even lower field might be assigned to the close proximity of the highly electronegative fluoride which is borne out by a substantial $^{19}$F$\rightarrow$P coupling ($^4J(31\text{P},^{19}\text{F}) = 15.3$ Hz, much larger than $^3J(31\text{P},^{19}\text{F}) = 3.5$ Hz in the 2-fluoro isomer where the F-P distance is larger, viz. ca. 295 pm [34]).

After all, we reconfirm our previous conclusion [16] that NMR does not provide any evidence for dative N$\rightarrow$P$^+$ bonding in the (DAN)phosphonium salts.

![Diagram](image-url)

This result has repercussions for the parent phosphate 5a and the related phosphines 5b, c. If, in DAN systems, even onium phosphorus does not exhibit electrophilic properties, an N$\rightarrow$P dative bond would be even less likely in the phosphines. And yet, such interaction has been inferred from the (averaged) N-P distances of 271.8 (5a) [8, 9], 278.6 (5b) [7, 9] and 283.4 pm (5c) [6, 9], on the basis that this is significantly shorter than the sum of the van der Waals radii ($\Sigma r_{vdW}$) of N and P (155 and 170 pm, respectively, according to Bateman’s scale [35]). This, however, is a property which all peri-disubstituted naphthalenes have in common, because the geometry of the naphthalene skeleton does not permit the substituents to go into van der Waals distance. By definition, for atoms considered as spherical particles, $\Sigma r_{vdW}$ is the equilibrium distance of repulsive forces and the notoriously weak van der Waals attractive forces [36]. Except for the obsolete model of atoms as hard (= non-compressible) spheres, the concept of $r_{vdW}$ is inapplicable wherever stronger forces are operative. This is ubiquitously so for intramolecular interatomic distances. The most striking (and generally
The rigidity of the naphthalene skeleton opposes deformation in either direction and thus the approximation of the peri-substituents to a bonding distance. Since bond angles are much more amenable to deformation than bond lengths are to stretching [42, 43], a strong covalent bond between the peri-substituents is capable of overcoming such resistance and of providing the energy required for the deformation of the natural bond angles, its length remaining unaltered. Thus, in acenaphthene, the C(sp³)–C(sp³) single bond, d = 154 pm, has the same length as in ethane, whereas the bond angles C(sp³)–C(1,8)–C(9) and C(1)–C(9)–C(8) are drastically decreased [43]. In a naphthalene of ideal geometry, the peri bonds emanating from C(1,8) are parallel, and the sum of the three peri angles is $3 \times 120° = 360°$. Since all covalent bonds between peri substituents (including “dative” and “hypercoordinate” bonds) are much shorter than the “natural” peri distance of ca. 247–250 pm [10], in such cases, the peri bonds are inclined towards each other, i.e. the sum of the three peri angles is < 360°, e.g. 328.9° in acenaphthene [43]. Hence, an experimentally found distance between the atoms bound to C(1,8) typical for the length of the envisaged bond would provide evidence for such bonding, and this should be paralleled by the sum of the three angles < 360°.

On the other hand, a peri distance of > 250 pm is typical for steric repulsion. This can, in principle, be minimized in two ways (or a combination of both): Either the naphthalene skeleton (including the atoms bound to C(1,8)) remains planar, and the three peri angles are widened (so that their sum becomes > 360°). Or the peri substituents evade to positions at opposite sides of the (average) naphthalene plane; this may or may not be accompanied by the loss of planarity of the C₁₀ skeleton. As a matter of fact, naphthalenes with non-bonding peri-substituents frequently make little use of the latter possibility [44]; if the former effect is the predominating one, the sum of the three angles > 360° is a supporting (though not independent) criterion for repulsion in addition to a distance > ca. 250 pm (for a proper assessment, the angle C(1)–C(9)–C(8), not taken into account by Schweizer et al. [2], is as essential as the exocyclic angles (peri-substituent)–C(1,8)–C(9)).

By turning to more appropriate standards of comparison than $\Sigma r_{vdw}$, we thus arrive at what we consider safe criteria whether attractive or repulsive forces are operating between any peri substituents [45]. In the phosphines 5a, b, the (averaged) N–P distances exceed the “ideal” distance of 250 pm by $\Delta d = 21.8$ (5a) and 28.6 pm (5b), hence quite substantially, and increasingly with increasing n, i.e. with increasing steric congestion in the peri region (formally, this trend continues to 5c, $\Delta d = 33.4$ pm; however, the X-ray structure has been obtained not from 5c, but from its hydrobromide [6] where the site of protonation, N or P, has not been established [46]). Correspondingly, the (averaged) sum of the three peri angles is 364.6° (5a) [47] and 363.8° (5b) [48]; i.e. the C(1)–P and the C(8)–N bonds diverge by 4.6 and 3.8°, respectively [49, 50]. The greater sterical hindrance in 5b thus does not manifest itself in these residual angles, but in a greater deviation from planarity, as borne out by the dihedral angles P–C(1)–C(8)–N (1.2° (average) in 5a [51]; 5.0 and 29.3° in 5b [52]). All this is in line with the increased steric congestion, but not with hypercoordination.

Phosphine sulfides are deprotonated mercaptophosphonium cations, so that the phosphorus should be more prone to hypercoordination than in phosphines. However, in the sulfide of 5b, the N–P distance d₈₋ₓ is 301.0 pm [7, 9], and the (average) sum of the three angles 365.2° [53], hence the residual angle, +5.2°, larger than in the parent phosphine 5b, and the dihedral angles P–C(1)–C(8)–N, 36.1 and 37.4° [53], are considerably larger. A
similar increase of \( d_{N-P} \) was observed in 5a (\( d_{N-P} = 271.8 \text{ pm} \)) and its benzylphosphonium salt 3cII (\( d_{N-P} = 283 \text{ pm} \) [9]), though, again, 3cII should be more apt to hypercoordination than 5a. Since in 5a, the global crowding in the peri space is smaller than in 5b, and, generally, the benzyl group is not a sterically demanding substituent, it is not a surprise that here, the increase, \( \Delta d = 11 \text{ pm} \), is smaller than from 5b to its sulfide (\( \Delta d = 22.4 \text{ pm} \)). Sterical hindrance in 5a has been reduced by insertion of ethylenyl groups into the \( P-\text{C}_{\text{Phenyl}} \) bonds; as a consequence, \( d_{N-P} \) is decreased by 9 pm [9], though it still surpasses the “ideal distance” by 12 pm. Revealing is the comparison of 5a, b with tris(2-dimethylamino)methyl-phenylphosphine. In the latter, the nitrogen is of the benzyl-di(methyl)amine type, hence a stronger nucleophile than in the DAN phosphines, and yet, \( d_{N-P} = 287 \text{ pm} \) [54] exceeds the “ideal” peri distance, and the sum of the three \( \text{N-C} \) and \( \text{Si-C} \) bonds is inclined towards the N–P repulsive bond from the nitrogen to the other \( \text{N-P} \) polarity. A counter-proof is provided by the global crowding in the \( \text{C}_{10} \) skeleton which permits such large N–P distances only in molecules with enhanced sterical hindrance such as the sulfide of 5b.

The typical domain of hypercoordinations of phosphorus is multiple-oxygen substituted, tetrahedral phosphorus. Therefore, diethyl DAN-phosphonate ought to be a much better candidate than 5a. And yet, \( d_{N-P} = 287 \text{ pm} \) [54] exceeds the “ideal” peri distance by 37 pm and is greater than in 5a by 12 pm; the sum of the three peri angles exceeds 360\(^\circ\) by as much as 8.6\(^\circ\) [54], and in addition, the dihedral angle \( P-\text{C}(1)-\text{C}(8)-\text{N} \), 15.8\(^\circ\) [54], is 13 times greater than in 5a.

The data thus meet all criteria of a repulsive N–P interaction, but none of those anticipated for a dative N–P bonding. A counter-proof is provided by DAN-tri(flouro)silane in which the three fluorine atoms create optimum conditions for pentacoordination at silicon. Here, the N–Si distance, 230.3 pm [55], is still 17 pm longer than the average N–Si distance in silatranes [56], but 21 pm shorter than the “ideal” peri distance, and the sum of the three peri angles falls short of 360\(^\circ\) by 6.6\(^\circ\) [55]; i.e., the N–C and the Si–C bonds are inclined towards each other by ca. 7\(^\circ\). Evidently, an attractive force is operative which is strong enough to overcome the resistance of the naphthalene against deformation [57].

In the phosphines 5a–c and their derivatives, then, the phosphorus is not hypercoordinate. In 5a, b and in the hydrobromide of 5c, the geometry around the phosphorus is (distorted) pseudo-tetrahedral (pseudo designating the lone pair as a pseudo-substituent), and the fact that these “tetrahedra” are “mono-capped”, “bicapped” and “tricapped” by the (\( \text{CH}_{3} \))\(_2\)N groups in 5a, b, 5c-HBr, respectively [6 - 9], is a necessity because of the geometry of the DAN group(s): The (\( \text{CH}_{3} \))\(_2\)N group(s) has/have no other choice.

We arrive at the conclusion that in these phosphines (and in many other DAN compounds), a dative bond from the nitrogen to the other peri substituent does not play any detectable role.

**Conclusion**

\( ^1\text{H} \) and \( ^{31}\text{P} \) NMR data of (DAN)phosphonium salts and the X-ray structures of the corresponding phosphines do not support the claim of dative N–P interaction. Geometrical considerations also render such interaction unlikely. We therefore discourage the use of formulae such as 3B’ as misleading.

**Experimental**

The NMR spectra were recorded on a Bruker AC 200 spectrometer at 200.132 MHz (\(^1\text{H}\)), 81.015 MHz (\(^{31}\text{P} \); ext. ref. \( 85\% \) \( \text{H}_2\text{PO}_4 \)) and 188.31 MHz (\(^{19}\text{F} \); ext. ref. \( \text{CCl}_3\text{F} \)) on solutions of ca. 0.2 mol/l solvent. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

(8-Fluoro-naphth-1-yl)(methyl)di(phenyl)phosphonium iodide (4dI): From a solution of 1.76 g (5.3 mmol) \((\text{8-fluoro-naphth-1-yl})\text{di(phenyl)}\)phosphine [1] and 0.40 ml methyl iodide in 25 ml benzene, kept at room temperature for 3 d, colourless crystals separated which were recrystallized from ethanol / benzene to give 2.11 g (80\%) of the hemi-ethanol solvate; m.p. 107 - 110 \(^\circ\) \( \text{C} \). \( \text{C}_{23}\text{H}_{19}\text{FIP} \text{O.5 C}_2\text{H}_5\text{OH} \) (492.3): Calcd. I 25.78, P 6.29; Found I 25.1, P 6.04%.

(Methyl)(naphth-1-yl)di(phenyl)phosphonium iodide (4cI) was obtained in the same way from (naphth-1-yl)di(phenyl)phosphine [60] and methyl iodide and recrystallized from dichloromethane / diethyl ether; yield 83\%, m.p. 216 - 218 \(^\circ\) \( \text{C} \). (Naphth-1-yl)di(phenyl)phosphine [59] reacted with ethyl bromoacetate and with benzylbromide in toluene to give the salts 4fII (89\% yield; m.p. 65 - 80 \(^\circ\) \( \text{C} \)) and 4gII (63\% yield; m.p. 312 - 318 \(^\circ\) \( \text{C} \)), respectively, which were used for the NMR measurements without further purification.
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(2-Fluoro-naphth-1-yl)(methyl)di(phenyl)phosphonium tetraphenylborate. From a solution of 1.58 g (4.8 mmol) (2-fluoro-naphth-1-yl)(di(phenyl)phosphine [1] and 0.40 ml methyl iodide in 25 ml benzene, kept at room temperature for 3 days, colourless crystals separated which liquefied when filtered off. The oily iodide iso-4dl was dissolved in 20 ml hot methanol, and a solution of 1.64 g (4.8 mmol) sodium tetraphenylborate in 15 ml methanol was added. The precipitate was recrystallized from acetonitrile to benzene to give 0.77 g (24%) of iso-4d-tetraphenylborate; m. p. 200 - 202 °C. Calcd. P 4.66; Found P 4.57%.

(8-Iodo-naphth-1-yl)(methyl)di(phenyl)phosphoronium iodide (4el) and tetraphenylborate: From a solution of 510 mg (1.16 mmol) (8-iodo-naphth-1-yl)-di(phenyl)phosphine [1] and 0.20 ml methyl iodide in 12 ml toluene, kept at room temperature for 10 d, slightly yellow crystals separated which were recrystallized from ethanol / diethyl ether to give 506 mg (75%) 4el; m. p. 167 - 169 °C. From 286 mg (0.49 mmol) 4el and 198 mg (0.58 mmol) sodium tetraphenylborate, both dissolved in methanol, 4e-tetraphenylborate precipitated which was recrystallized from acetonitrile / ethanol; yield 164 mg (43%); m. p. 185 - 187 °C. Calcd. I 24.0, P 3.92; Found P 4.01; Found P 16.5, P 3.95%.

Acknowledgements

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[6] C. Chuit, R. J. P. Corriu, P. Monforte, C. Reyé, J.-P. Declercq, A. Dubourg, Angew. Chem. 105, 1529 (1993); Angew. Chem. Int. Ed. Engl. 32, 1430 (1993). In fact, no X-ray data of 5c have been obtained. The published structure is that of an ethanol solvate of a hydrobromide of 5c. Whether this is a tertiary phosphonium salt, a tertiary ammonium salt or a proton sponge type salt with a [N...H...P]+ substructure, is not known. In the first case, it was irrelevant to the question of hypercoordination at pseudo-tetracoordinate (i.e. phosphine) phosphorus, in the second case, to the question of pseudo-heptacoordination, and in the third case, to both.
[9] C. Chuit, C. Reyé, Eur. J. Inorg. Chem. 1847 (1998). In view of the similarity of the $\Delta G^\circ$ values, we suggest that the $^1$H NMR non-equivalence of the N-methyl groups reported here and by M. Chauhan, C. Chuit, C. Fruchier, C. Reyé, Inorg. Chem. 38, 1336 (1999), for many DAN-P compounds (and elsewhere for DAN-Si compounds) has the same origin as in the carbinal (DAN)2CH(OH) [10, 11], i.e., is due to hindered rotation, hence no evidence for N=P(Si) bonding. In our opinion, the proposed mechanism of a nondissociative ligand exchange [with respect to the alleged N=P bonds; $\Delta G^\circ = ca. 90 \text{kJmol}^{-1}$ for 5b] [7] and 5c (Eur. J. Inorg. Chem., loc. cit., p. 1852) derived from the N=P distances.
[12] To cope with this shortcoming, the concept of a continuous range of bond lengths between the sum of the van der Waals radii, $\Sigma_{vdw}$, and of covalent bond lengths, $\Sigma_{dco}$, has been devised; cf., e. g., R. O. Day, T. K. Prakash, R. R. Holmes, H. Eckert, Organometallics 13, 1285 (1994), p. 1290; T. K. Prakash, S. Srinivasan, A. Chandrasekaran, R. O. Day, R. R. Holmes, J. Am. Chem. Soc. 117, 10003 (1995), p. 10006. We find it hard to reconcile this concept with the experimental experience that bond lengths tend to be strongly resistant to stretching. Forced to increased interatomic distances of even

[13] For the definition of a *dative bond* and its symbol, see, e. g., K. Purcell, J. C. Kotz, Inorganic Chemistry, p. 68, W. B. Saunders Company, Philadelphia 1977. Note that the *dative bond* is a sort of mnemotechnical device rather than a special kind of two electron bond, and that, e. g. in *PF6-*, there is no dichotomy of “normal” and “hypercoordinate” bonds.


[17] In *loc. cit.* [8], the discussion of our paper [16] is confined to the statement that “the possible existence of intramolecular N—P interactions in these compounds has rarely been considered”, and to the melting points of **3Al**, **5a** and the phosphine sulfide of **5a**. Cf. *loc. cit.* [6, 7, 9].

[18] Schiemenz, Papageorgiou [16], Table I, entry 7.


[20] Schiemenz, Papageorgiou [16], Table I, entry 6.

[21] Note that in methylene chloride, the figures are 3.00, 2.88 (Carre et al., p. 188), 4.2 - 4.6, 3.2 - 3.6 (2 stereoisomers: Carre et al. [22], p. 192), the additional highfield shift can be rationalized as being due to an (averaged) position of these protons above the second C10 skeleton and, hence, to increased “aromatic shielding”.


[27] If any interatomic distance d < \( \Sigma r_{vdw} \) is evidence of hypercoordination, then H in CH4 is tetracordinate.

[28] According to Holmes’ procedure [12], the tetrahedral character (in analogy to Holmes’ TBP and octahedral characters) of hydrogen in methane is 63%.

[29] Pauling [37], p. 167.

[30] According to Holmes’ procedure [12], 52% TBP character for C(1,3), the five coordinating atoms of C(1) being three H atoms, C(2) and – at a larger, though sub-\( v d \)er Waals distance – C(3). Note that the geometry around C(1), conventionally described as a (necessarily slightly distorted) tetrahedron, can also be described as a “strongly distorted trigonal bipyramid” in which the central atom is displaced from the equatorial plane towards one of the apices and in which the other apex is occupied by an atom (here: C(3)) at much larger distance (“in which one of the apical bonds is strongly elongated though still considerably shorter than \( \Sigma r_{vdw} \)” in the terms of the advocates of hypercoordination).

[31] For this reason, from the N-Si distances collected by H. Bock, Z. Havlas, V. Krenzel, Angew. Chem. **110**, 3305 (1998), Angew. Chem. Int. Ed. Engl. **37**, 3163 (1998), all those obtained from DAN silanes have to remain out of consideration. Note that *stirol* is not an N-methyl compound (G. Klebe, J. W. Bats, K. Hensen, Z. Naturforsch. **38b**, 825 - 829 (1983)) and, consequently, the N-S-\( \text{amino} \)-Si bond (d = 176 pm) is a normal (alkyl)(aryl)(silyl)amine bond, not a *dative* hypercoordinate bond. The calculations on the NH3/\( \text{SiH}4 \) system performed by the authors...
naturally have no bearing on the deformation of peri-substituted naphthalenes.


[45] Hydrogen bonds between peri substituents represent a special case which we intend to deal with elsewhere.


[47] Data obtained from Chuit et al. [8], Table 4.

[48] Data obtained from Chauhan et al. [7], Table 7. For the hydrobromide of 5c, the pertinent data have not been published [6].

[49] 6.3° (average) in the hydrobromide of 5c (data obtained from the supplementary material of loc. cit. [6]).

[50] Both in 5a and 5b (as well as in many other DAN compounds), the angle N–C(8)–C(9) is smaller than 120°. However, what matters is only the sum of the three angles > 360°, i.e., the residual or splay angle (cf. T. Katoh, K. Ogawa, Y. Inagaki, R. Okazaki, Tetrahedron 53, 3557 (1997)). If two angles, or even one angle, are (is) sufficiently large, the geometry is able of tolerating the third one (or even two angles) to be smaller than 120°. Cf., e.g., 1,8-difluoronaphthalene (A. Meresse, C. Courseille, F. Leroy, N. B. Chanh, Acta Crystallogr. B 31, 1236 – 1241 (1975)); F(1)–C(1)–C(9) 118.8°, F(2)–C(8)–C(9) 118.2°, C(1)–C(9)–C(8) 126.5, sum 363.5°, hence splay angle +3.5°; accordingly, d(F-F) = 258.4 pm, i.e., 11.6 pm longer than the “ideal distance” [10] (though 41.6 pm shorter than Σr_{C-F} = 300 pm [35] so that by Holmes’ procedure [12] for fluorine a hypercoordination character of 26.7% is calculated (with Σr_{C-F} = 144 pm; cf. Staab [4], p. 193)). For similar phenomena, cf. F. Riedmiller, A. Jockisch, H. Schmidbaur, Organometallics 17, 4444 (1998), for a more detailed analysis of the force vectors operating in peri-substituted naphthalenes, Clough et al. [44].

[51] Obtained from the data in loc. cit. [8], Table 4 (cf. ibid., p. 172: “no more than 2°” for “N–C(8)–P...C(1)”).

[52] Obtained from the data in loc. cit. [7], Table 7 (cf. ibid., p. 174: “the dihedral angle C13–P...N2–C21 of 27°” [C13 = C(1), C21 = C(8), N2 = N of the more deformed DAN group]).

[53] Obtained from loc. cit. [7], Table 8.


