peri-Interactions in Naphthalenes, 10 [1]. In Search of Independent Criteria for N⟶P Bonding: Protonation Studies on (8-Diethylamino-naphth-1-yl)-diphenyl-phosphine

Günter Paulus Schiemenz, Christian Näther, and Simon Pörksen

Institut für Anorganische Chemie der Universität, 24098 Kiel, Germany

Reprint requests to Prof. Dr. G. P. Schiemenz. Fax: +49 (0)431 880 1558.
E-mail: schiemenz@ac.uni-kiel.de

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Enhancement of the basicity of the amino group in (8-dialkylamino-naphth-1-yl)-diphenylphosphines diverts protonation from the P to the N atom. Thus the cation 8-$Et_2N^+(H)$-$C_{10}H_6$-PPh_2 becomes available whose ^1H and ^{31}P NMR spectra provide arguments against dative N→P interactions in the phosphines and their quaternary phosphonium salts. Likewise, the X-ray structure of 8-Et_2N-$C_{10}H_6$-PPh_2 does not indicate such interactions.

Key words: N→P Bonding, NMR Protonation Shifts, $d(N\cdots P)$ Distances

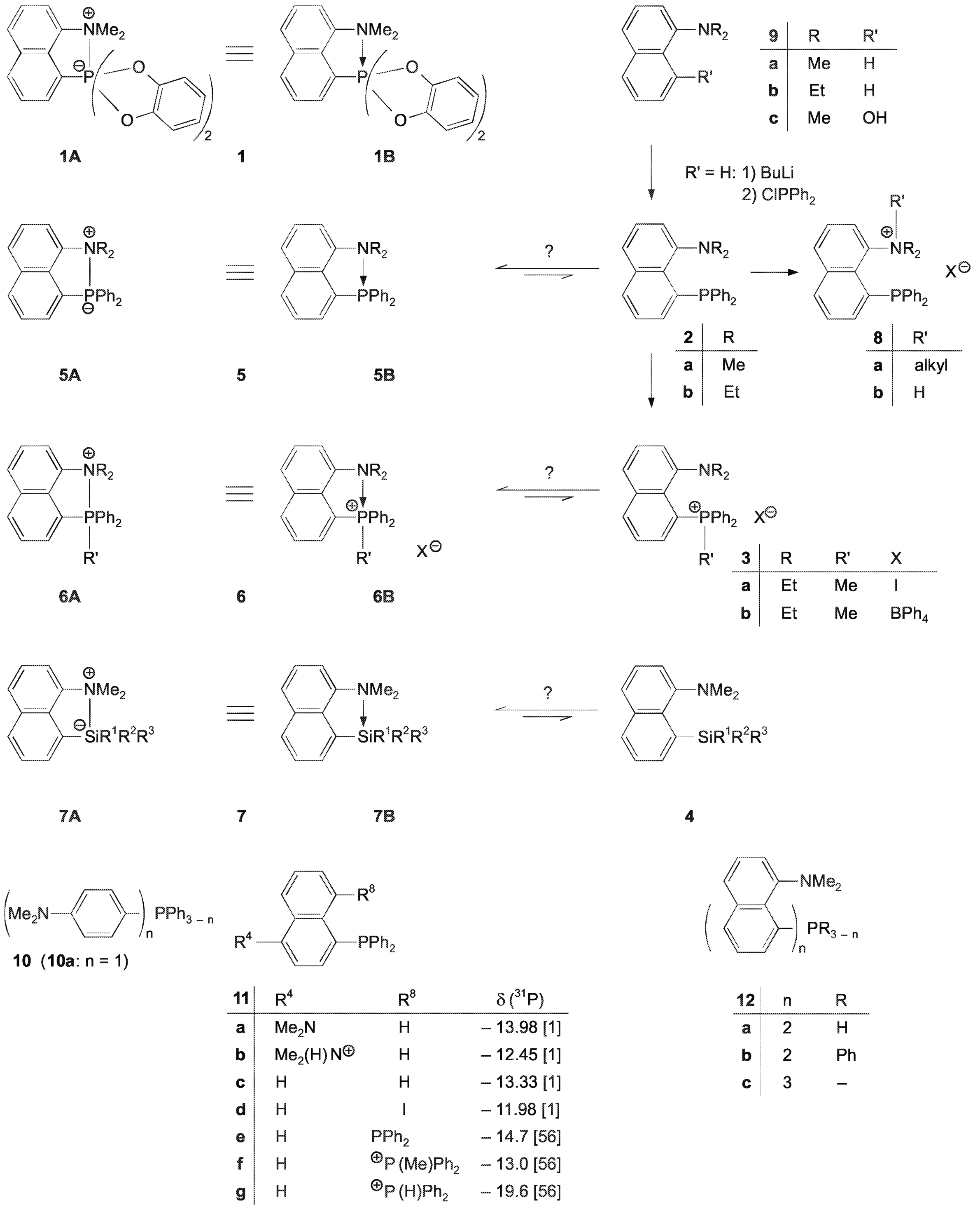
Introduction

In 8-dialkylamino-naphth-1-yl-phosphorus compounds (“DAN-**P**”), suitably substituted phosphorus is able to overcome the geometric resistance of the C_{10} skeleton and to engage in a N−P bond of conventional length (213.2 pm in **1**) [2]. Concomitantly, the *peri* bonds P−C(1) and N−C(8) are inclined towards each other (splay angle −11.5° in **1**). The new bond is one of four two-electron bonds emanating from the N atom which thereby has ammonium character. The P atom may (as in **1A**) or may not be the site of a negative charge. The N−P bond is conveniently described as a covalent single bond whose two electrons are donated by the N atom as a nucleophile and accepted by the P atom as an electrophile. It is therefore adequately called a *dative bond* and hence may be depicted by the common symbol of the latter, hence as N→P, as in **1B**, in analogy of the familiar representation of the amine oxides by the formula $R_3N{\rightarrow}O$ [3].

On the other hand, the structures of DAN-phosphines **2** [1, 4 – 7], DAN-phosphonium salts **3** [6 – 11], and DAN-silanes **4** [12 – 14] exhibit the criteria of steric repulsion between the *peri* substituents [1, 2, 11, 15 – 20], *viz*. interatomic distances $d(N\cdots P/Si)$ = *ca*. 280 ± 20 pm [1, 4 – 14] and positive splay angles [1, 2, 15, 17 – 21]. Nevertheless, it has been claimed that in these compounds a dative interaction (albeit a weak one [4, 7, 8, 12b, 13, 22]) is operative which consistently had been expressed by the formulae **5 – 7B** with the N→P/Si symbol [4, 5, 7 – 10, 12, 13, 22 – 24]. The claim rests exclusively on the fact that $d(N\cdots P/Si)$ is smaller than the sum of the respective van der Waals radii, $\Sigma r(vdW_{N,P/Si})$ [4 – 10, 12b, 25]. While the rigidity of the C_{10} skeleton renders Σr(vdW) an inappropriate reference for *peri*-substituted naphthalenes [1, 2, 11, 15, 17 – 20], it has been observed that in such silanes the criteria of steric hindrance are less pronounced than in several 1,8-disubstituted naphthalenes which lack the possibility of intersubstituent donor / acceptor interaction [15]. Though alternative rationalizations are at hand, the question has been raised whether the phenomenon may reflect an attractive contribution to the overall effect in which the repulsive one dominates [15, 26].

Obviously, no answer can be provided solely by recourse to $d(N\cdots P/Si)$. It is indispensable to search for independent criteria which respond more specifically to dative N→P/Si bonding. The decisive feature is the availability of the lone pair at the N atom for *peri* interactions. Insight into its role may be expected if it could be blocked with as little change in the steric situation as possible and respective derivatives studied for comparison.

In DAN-phosphines **2**, the nucleophilicity of the N atom could be eliminated by the use of the lone pair for a new σ-bond, hence by turning to 8-ammonio-substituted naphth-1-yl-phosphines (**2** → **8**). A significant



9	R	R'
a	Me	H
b	Et	H
c	Me	OH

2	R
a	Me
b	Et

8	R'
a	alkyl
b	H

3	R	R'	X
a	Et	Me	I
b	Et	Me	BPh_4

11	R^4	R^8	δ(^{31}P)
a	Me_2N	H	– 13.98 [1]
b	$Me_2(H)N^{\oplus}$	H	– 12.45 [1]
c	H	H	– 13.33 [1]
d	H	I	– 11.98 [1]
e	H	PPh_2	– 14.7 [56]
f	H	$^{\oplus}P(Me)Ph_2$	– 13.0 [56]
g	H	$^{\oplus}P(H)Ph_2$	– 19.6 [56]

12	n	R
a	2	H
b	2	Ph
c	3	–

Scheme 1.

charge transfer from the donor D to the acceptor A is typical for *dative bonds* [27] and should therefore be a prominent feature of the DAN-phosphines if N→P interaction played the alleged role. More clearly than in the formula D→A, such transfer is expressed (though possibly overemphasized [28]) in the alternative formula $D^+{-}A^-$ (*e. g.* **1A** and $R_3N^+{-}\overline{\underline{O}}|^-$ rather than **1B** and $R_3N \rightarrow O$ for **1** and the amine oxides, respectively), hence **5A** for the DAN-phosphines [29]. If **5A** were an adequate formula of the DAN-phosphines, the latter would share an electron depletion at the N atom with their ammonium derivatives **8**. This should be reflected by similar positions of the ^{1}H NMR signals of the protons within the R groups at N, $\delta(N-C-{}^1H)$. If, on the other hand, N→P interaction played no significant role, the DAN-phosphines and their ammonium derivatives should differ to a similar degree as 1-dimethylamino-naphthalene (**9a**, $\delta(N-C-{}^1H) = 2.91$ in $CDCl_3$ [30]) and its methiodide ($\delta(N-C-{}^1H) = 4.12$ in CF_3COOH [31]) do. To be sure, aromatic ring current effects of the C_{10} skeleton and of the phenyl substituents at the P atom have a strong impact on the signal positions [2, 15, 17, 30], but they can be assumed to be roughly constant provided that the steric changes are kept at a minimum.

In principle, quaternization of the R_2N group (**2** → **8a**) would serve the envisaged purpose, but it would significantly enhance the steric congestion within the *peri* space. *E. g.*, a trimethylammonio group would sterically resemble a *tert*-butyl group which is known to cause exceptional steric hindrance [32]. N-alkylation would therefore cause a stronger deformation of the C_{10} skeleton (including an increased distance $d(N\cdots P)$) which might have repercussions on $\delta(N-C-{}^1H)$. In addition, replacement of a bond between N and P (Pauling electronegativity 2.1 [33, 34]) in **5** by a bond between N and C (Pauling electronegativity 2.5 [33]) in **8a** would be expected to induce a downfield shift of $N-C-{}^1H$ signals [35] which has no bearing on the problem under investigation.

N-*Protonation* would be preferable for several reasons. Hydrogen and phosphorus happen to have equal electronegativities (2.1 [33]) so that the effect of the replacement should be kept at a minimum. Sterically, the $Me_2(H)N^+$ group would resemble an isopropyl group which in a hetera-naphthalene has been shown to fit reasonably well into the *peri* space in a similar manner as a Me_2N group does in DAN-**P**/**Si** compounds [19]. While **5A/B** lacks a basic nitrogen function, an equilibrium **5A/B** ⇆ **2** would enable even small quantities of **2** to be trapped by N-protonation (**2** → **8b**). A similar degree of ammonium character of the N atom in the neutral species **5A/B** and in the ammonium salt **8b** would cause the protonation shift of $N-C-{}^1H$ NMR signals to be unusually small.

Unfortunately, both N-alkylation and N-protonation of DAN-phosphines face severe preparative difficulties. **9a** is not easily methylated [36]; *peri* substituents further reduce the nucleophilicity of the Me_2N group [37, 38]. On the other hand, triarylphosphines exhibit a much greater nucleophilicity towards alkyl halides than N,N-dimethylanilines. This is borne out by the exclusive P-alkylation of tertiary (4-dimethylamino-phenyl)-phosphines (**10)** [39] and of (4-dimethylamino-naphth-1-yl)-diphenylphosphine (**11a**) [30]. 8-Trialkylammonio-substituted (naphth-1-yl)-phosphines **8a** thus remain out of reach.

We therefore focussed our attention on selective N-protonation of DAN-phosphines. N,N-dimethylanilines are much more basic than most tertiary phosphines. *E. g.*, **10a** and **11a** are first protonated at the N atom [1, 40]. However, DAN-phosphines exhibit an extraordinary P-basicity and are protonated exclusively at the P atom [1, 6]; as with the *proton sponge* [41], bis-protonation of both basic centres does not take place [1].

To achieve N-protonation, it would be essential either to decrease the basicity of the phosphino function or to increase the basicity of the amino group. Secondary phosphines R_2PH are frequently considerably weaker bases than similar tertiary phosphines R_3P [42]; hence, phosphines (DAN)(R)PH looked promising. However, **12a** exhibited an unusual P-basicity and was again protonated at the P atom [1]. It remained to enhance the N-basicity of DAN-phosphines. This would likewise improve the conditions for dative N→P bonding, so that respective phosphines **2** deserve particular attention.

Results and Discussion

Though the phenomenon defies a straightforward explanation, it is known that N,N-dialkylanilines $ArNR^1R^2$ have a maximum basicity for $R^1 = R^2 = Et$ [43]. It is also shown by the N,N-dialkyl-*o*-toluidines ($2\text{-}MeC_6H_4NR_2$, R = Et/Me: $\Delta pK_a = 1.32$ [43]). We therefore turned to (8-di*ethyl*amino-naphth-1-yl)-diphenylphosphine (**2b**), which was obtained in 37% yield by lithiation of 1-diethylamino-naphthalene (**9b**) in the 8-

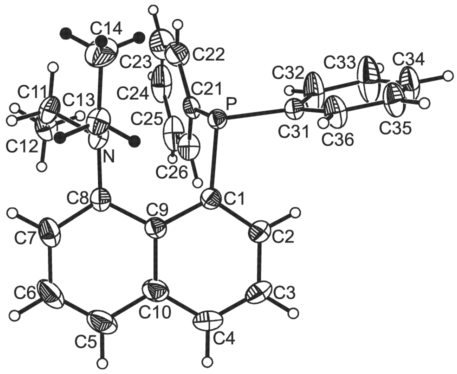


Fig. 1. Crystal structure of **2b** with labelling and displacement ellipsoids drawn at the 50% probability level.

position and subsequent reaction with chloro-diphenylphosphine (*cf.* Scheme 1). Reaction with iodomethane proceeded smoothly at room temperature and afforded the quaternary phosphonium iodide **3a** in quantitative yield from which the tetraphenylborate **3b** was prepared.

A single crystal X-ray structure determination of **2b** revealed a structure which closely resembles that of the corresponding N,N-di*methyl*amino compound **2a** [5]. The distance *d*(N···P), 280.3 pm, is *ca.* 30 pm longer than estimated for a DAN-phosphine of ideal geometry [1, 2, 11, 16 – 20, 44] and slightly longer than in **2a** (270.6/272.9 pm in two independent molecules [5]), but almost identical with *d*(N···P) = 278.0/279.2 pm in **12b** [4] and slightly shorter than *d*(N···P) = 282.0/282.8/288.5 pm in **12c** [6]. The gradual increase **2a** < **12b** < **2b** < **12c** is likely to reflect enhanced steric hindrance, though the additional carbon atoms of the ethyl groups in **2b** reside outside the *peri* space and thus do not visibly increase the congestion within it (see Fig. 1). The bay angles P–C(1)–C(9) (122.5°), C(1)–C(9)–C(8) (125.0°) and N–C(8)–C(9) (119.4°) yield a splay angle of +6.9° which is again an indication of considerable steric hindrance. As elsewhere, C(1)–C(9)–C(8) is the largest and N–C(8)–C(9) the smallest angle [17,20]. Likewise, the non-bonding interatomic distance *d*(C(1)···C(8)) = 255.5 pm exceeds the distance in naphthalene of ideal geometry by 8.7 pm [2, 11, 15], whereas the opposite *peri* distance *d*(C(4)···C(5)) = 244.3 pm is slightly compressed [45]. Compound **2b** is thus a flawless example of a 1,8-disubstituted naphthalene with repulsive steric interactions between the *peri*-substituents where no N→P dative bond is indicated.

The C_{10} skeleton is almost planar, and both the N atom and the P atom reside almost in the C_{10} plane (torsional angles P–C(1)–C(9)–C(8) −0.9°, N–C(8)–C(9)–C(1) −5.8°). Consequently, the N···P interatomic connecting line is also very close to the C_{10} plane (N···P–C(1)–C(9) +3.1°, P···N–C(8)–C(9) +6.4°). On the other hand, the directions of the N–CH_2 bonds imply that the lone pair at N does *not* point towards the P atom: One of them is virtually perpendicular to the C_{10} plane (C(13)–N–C(8)–C(9) −90.9°), the other one in the anticlinal sector with respect to the C(1)···C(8) connecting line (C(11)–N–C(8)–C(9) +145.8°) so that the occupied orbital at N would be estimated to reside approximately at the borderline between the synperiplanar and the synclinal sectors [46]. Of the two P–C_{Ph} bonds, one is coplanar with the C_{10} plane in the sterically most favourable antiperiplanar direction (C(31)–P–C(1)–C(9) −179.7°), the other one not far from orthogonality in the synclinal sector (C(21)–P–C(1)–C(9) −77.1°) (hence, again in a sterically favourable position). The lone pair at P then is located in the synclinal sector at the opposite face of the C_{10} plane so that Coulomb repulsion of the lone pairs is minimized. The joint effects of Coulomb repulsion and the steric requirements then account for the conformation of the substituents, whereas no involvement of the N lone pair in the N···P interaction is indicated.

The angle C(1)–P–C(31) (*i. e.* C(1) of the antiperiplanar phenyl group), 102.9°, is within the range of the C–P–C angles in Ph_3P (102.1 – 103.6° [47]). Because of *d*(P–C(1)) > *d*(N–C(8)) the angle N···P–C(1) is smaller than 90°, *viz.* 76.3°. As a trivial geometric consequence, the atoms N, P and C(31) are aligned virtually linearly in the C_{10} plane (angle N···P–C(31) 177.1°). This linearity would permit to describe the environment of the P atom as a distorted trigonal bipyramid with N and C(31) in apical positions [48] and with a much deformed equatorial plane in which the P lone pair occupies one of the coordination sites [17,20,49]. However, the arrangement has nothing to do with pentacoordination; it rather suffices to invalidate conclusions in favour of attractive N/Te and F/Se interactions in the ditelluride (8-Me_2N- $C_{10}H_6$-Te-$)_2$ and an aryl-(8-fluoro-naphth-1-yl)-selenide derived from the “T-shaped alignments” of N···Te(C(1))–Te [50] and F···Se(C(1))–C_{Ar} [51].

NMR spectra of the isolated compounds

In the ^{31}P NMR spectrum of **2b**, the signal position at low field (δ = +0.24 ppm) is virtually identical with that of **2a** (δ = +0.54 ppm [1,44]). δ = +24.46 ppm of **3b** is unconspicuous; $^2J(^1\mathrm{H}, ^{31}\mathrm{P})$ = 13.5 Hz of the $\mathrm{P{-}C^1}H_3$ signal in the ^{1}H NMR spectrum is proof that the methylation had occurred at the P centre.

In **2b** and its methyl-phosphonium salts **3a**,**b**, the geminal protons of the $\mathrm{N{-}CH_2}$ groups are diastereotopic due to restricted rotation around the N–C(8) bond [20]. Correspondingly, the $\mathrm{N{-}C^1}H_2$ region of the ^{1}H NMR spectrum of **2b** consists of two doublets of quartets, positioned at slightly higher field than the $\mathrm{N{-}C^1}H_2$ quartet in **9b** (δ = 3.15): $\mathrm{H^A}$: δ = 2.85, $\mathrm{H^B}$: δ = 2.98, $^2J(^1\mathrm{H^A}, ^1\mathrm{H^B})$ = 13.0 Hz, $^3J(^1\mathrm{H^{A,B}}, \mathrm{C^1H_3})$ = 7.1 Hz. Upon quaternization at P, both multiplets are shifted to *higher* field: **3a**: $\mathrm{H^A}$: δ = 2.28, H^B: δ = 2.76, $^2J(^1\mathrm{H^A}, ^1\mathrm{H^B})$ = 13.3 Hz, $^3J(^1\mathrm{H^{A,B}}, \mathrm{C^1H_3})$ = 7.1 Hz. This phenomenon had previously been observed with **2a** and its alkyl phosphonium iodides and ascribed to a change in the ring current effect of the phenyl groups attached to the P atom [30]. As in the $\mathrm{Me_2N}$ compounds, a significant counterion induced shift (CIS) effect [52] of the $\mathrm{BPh_4^-}$ anion is restricted to the $\mathrm{P{-}C^1}H_3$ protons (**3a/b**: $\Delta\delta$ = 0.51 ppm), whereas the $\mathrm{N{-}C^1}H_2$ signals are not much affected (**3a** → **3b**: 2.28/2.76 ppm → 2.21/2.70 ppm). The different sensitivity demonstrates that the P atom is the centre of the positive charge [30].

NMR protonation shifts

Protonation studies were performed as previously described [1]. In the ^{1}H- coupled ^{31}P NMR spectrum of **2b**, addition of 0.96 equivalents of *p*-toluenesulfonic acid (TsOH) caused a highfield shift of the ^{31}P signal from +0.24 to −15.52 ppm. No $^1J(^{31}\mathrm{P}, ^1\mathrm{H})$ coupling due to P-protonation was observed; the ^{31}P resonance was recorded as one somewhat broadened signal in which the $^3J(^{31}\mathrm{P}, ^1\mathrm{H})$ coupling with the four 2,6-H's of the phenyl rings and the 2-proton of the DAN group was not resolved.

The value δ = −15.52 ppm is incompatible with a phosphonium structure, but similar to the values observed in other (naphth-1-yl)-diphenyl-phosphines in which no downfield $\mathrm{R_2N}$ effect is operative [44] (*e. g.*, **11a**–**g** : δ = −11.98 to −19.6; *cf.* Scheme 1). On the one hand, the highfield shift of $\Delta\delta$ = 15.76 ppm upon N-protonation demonstrates the decisive role of the N lone pair for the unusual δ values of the phosphines **2a**,**b** and **12b**,**c** [44]. On the other hand, their signal positions at very low field exclude phosphorane or λ^6-phosphate structures and hence a *bonding* N→P interaction. The phenomenon resembles the very large coupling constants of *peri*-bound ^{19}F and ^{31}P for which a theory has been developed which assumes orbital interactions which, however, are not bonding [53].

In the ^{1}H NMR spectrum, the sharp $\mathrm{N{-}CH_2{-}C^1}H_3$ triplet experienced a downfield shift of $\Delta\delta$ = 0.32 ppm. The $\mathrm{N{-}C^1}H_2$ protons gave two ill-resolved multiplets at 3.83 and 4.00 ppm which indicate protonation shifts of 1.02 and 0.98 ppm, larger than in the *proton sponge* ($\Delta\delta$ = 0.80 ppm [38a]), almost double as large as in **11a,b** ($\Delta\delta$ = 0.56 ppm [1]) and more similar to the quaternization shift $\Delta\delta$ = 1.21 ppm of the $\mathrm{N{-}C^1}H_3$ signals of **9a** and its methiodide [30,31]). The positions of the $\mathrm{N{-}C{-}^1}H$ multiplets of N-protonated **2b** closely resemble $\delta(\mathrm{C^1}H_3)$ = 3.75 and 4.01 for the $\mathrm{N^+(H)Me_2}$ and the $\mathrm{N^+Me_3}$ groups, respectively, in 8-$\mathrm{Me_3N^+\text{-}C_{10}H_6N^+(H)Me_2}$ [38b]. The obvious conclusion is that in the phosphine **2b**, the N atom does not bear a positive charge.

When ^{1}H NMR spectra of **2b** in the presence of 0.96 equiv. of TsOH were recorded at lower temperatures at intervals of 10 K down to 243 K, no sharpening of the $\mathrm{N{-}C^1}H_2$ multiplets was observed. They rather merged into one unresolved signal at δ = 4.05 (243 K), because the highfield multiplet migrated to lower field faster than the lowfield multiplet. At lower temperatures, the resolution of the $\mathrm{N{-}CH_2{-}C^1}H_3$ triplet deteriorated; the phenomenon may be caused by the freezing of rotation around further single bonds (the P–C(1) bond as a first choice) and hence the formation of diastereomers. The $\mathrm{N{-}C^1}H_2$ absorption of a minor diastereomer may account for a new, non-resolved signal of small intensity at *ca*. 3.82 – 3.85 ppm (243 – 263 K).

When addition of $\mathrm{CF_3COOH}$ to the **2b**/0.96 equiv. of TsOH solution enhanced the amount of acid to 10.0 equivalents, the ^{1}H-coupled ^{31}P NMR spectrum exhibited two sharp signals of roughly equal intensities at −14.89 and −15.81 ppm. Again, the signal positions exclude P-protonation; in addition, $\Delta\delta$ = 74 Hz does not qualify for a $^1J(^{31}\mathrm{P}, ^1\mathrm{H})$ coupling constant. No $^3J(^{31}\mathrm{P}, ^1\mathrm{H})$ couplings were visible. The signals may be ascribed to two diastereomers. This is corroborated by the ^{1}H 200 MHz NMR spectrum: A sharp $\mathrm{N{-}CH_2{-}C^1}H_3$ triplet at 1.09 ppm (^3J = 7.2 Hz) is accompanied by a less intense, equally sharp triplet, δ = 1.00 (^3J = 7.2 Hz). The $\mathrm{N{-}C^1}H_2$ absorption consists of two multiplets which tentatively can be interpreted as the almost perfect superposition of the lowfield multiplets of both stereoisomers, centered at δ = 3.80, and a partial superposition of the highfield multiplets, that of the major isomer being centred at δ = *ca.* 3.53 and that of the minor isomer at δ = *ca.* 3.44. These signal positions would correspond to protonation shifts of $\Delta\delta$ = 0.82, 0.68 and 0.59 ppm, respectively, still exceeding that of **11a**,**b**. The decrease is likely to reflect a solvent effect, as *ca.* 90 mg of CF$_3$COOH had been added to 0.6 ml of CDCl$_3$. The occurrence of only one, but broadened ^{31}P NMR signal in the spectrum of **2b** + 0.96 equiv. of acid may be attributed to an interconversion process between the stereoisomers. Since no such isomerization is observed at high acid concentrations, it is suggested that it proceeds via **2b**, hence, that the steric stability of **2b** is enhanced by N-protonation. Conceivably, the cancellation of inversion at the N atom could play a role. Finally, hydrogen bonding of the cation with the excess acid may also be involved.

Table 1. Selected distances (pm), angles (°) and torsion angles (°) for **2b**.

P···N	280.3(2)	P–C1	185.2(2)
C8–N	143.8(2)	N–C11	147.1(2)
N–C13	146.7(4)	C11–C12	151.1(3)
C13–C14	150.2(4)	P–C31	184.8(2)
P–C21	182.4(2)		
C1–P–C21	101.4(1)	C8–N–C11	115.0(2)
C1–P–C31	102.9(1)	C8–N–C13	106.0(2)
C21–P–C31	99.5(1)	C11–N–C13	111.2(2)
C9–C1–P	122.5(2)	N–C11–C12	114.5(2)
C9–C8–N	119.4(2)	N–C13–C14	112.3(3)
C1–C9–C8	125.0(2)		
P–C1–C2–C3	179.4(3)	N–C8–C7–C6	−177.2(2)
P–C1–C9–C10	178.5(2)	N–C8–C9–C10	175.2(2)
P–C1–C9–C8	−0.5(3)	N–C8–C9–C1	−5.8(3)
C21–P–C1–C2	104.4(2)	C11–N–C8–C7	−37.4(3)
C31–P–C1–C2	1.8(2)	C13–N–C8–C7	85.9(3)
C21–P–C1–C9	−77.1(2)	C11–N–C8–C9	145.8(2)
C31–P–C1–C9	−179.7(2)	C13–N–C8–C9	−90.9(3)
C2–C1–C9–C8	178.1(2)	C8–N–C11–C12	−55.4(3)
C3–C4–C10–C5	179.1(3)	C8–N–C13–C14	175.3(3)
C6–C5–C10–C4	179.4(3)	C11–N–C13–C14	−59.0(4)
C7–C8–C9–C1	177.4(2)	C13–N–C11–C12	−175.8(3)

Conclusion

The NMR data of **2b**, its N-protonated derivative and its quaternary phosphonium salts **3a**,**b** indicate that neither in **2b** nor in the quaternized compounds there is a significant charge transfer from the N to the P atom (and *vice versa*). The data thus provide an independent argument for the conclusion reached in a recent NMR investigation of **12a** that in DAN-**P** compounds interatomic distances *d*(N···P) of *ca.* 280 pm (much shorter than the sum of the van der Waals radii of N and P) occur which are not the consequence of dative N→P interactions [1]. The conservative formulae **2** and **3** are entirely satisfactory representations of DAN-phosphines and DAN-phosphonium salts whereas alternative formulae such as **5A**,**B** and **6A**,**B** are misleading. We therefore discourage the use of such formulae.

Experimental Section

The NMR spectra were recorded as described previously [1]. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

(8-Diethylamino-naphth-1-yl)-diphenyl-phosphine (**2b**): A commercial 1.6 M solution of *n*-butyllithium in *n*-hexane (10.0 ml) was added to 1-diethylamino-naphthalene (3.208 g, 16.1 mmol, prepared from 1-amino-naphthalene and diethyl sulfate; b.p. 181 – 184 °C/20 torr) in anhydrous diethyl ether (5 ml). Within 27 d, the solution turned red. Upon stirring for 30 min, yellow crystals of 8-diethylamino-naphth-1-yl lithium separated. After additional 6 d (without stirring) the liquid was removed with a syringe and replaced by 10 ml of diethyl ether. Then 1.05 ml (5.85 mmol) of chloro-diphenylphosphine was added within 10 min by means of a syringe. After stirring at room temperature for 19 h, the mixture was hydrolyzed with 10 ml of water and 3 ml of 2 N NaOH. The phosphine was extracted into 30 ml of toluene, the solution filtered through a column of magnesium sulfate and silica gel and evaporated. The residual oil (1.715 g) was dissolved in 20 ml of boiling ethanol. Upon cooling, 824 mg (37%) of yellow crystals separated. M. p. 119 – 121 °C. – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.70 (t, ^{3}J(H, H) = 7.1 Hz, 6H, C–C$^{1}H_3$), 2.85 (dq, ^{2}J(H^{A}, H^{B}) = 13.0 Hz, ^{3}J(H, H) = 7.1 Hz, 2H, N–C–$^{1}H^{A}$), 2.98 (dq, ^{2}J(H^{A}, H^{B}) = 13.0 Hz, ^{3}J(H, H) = 7.1 Hz, 2H, N–C–$^{1}H^{B}$), 6.88 – 7.79 (m, 16H, arom. protons). – ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$): δ = 9.62 (d, ^{6}J(H, P) = 1.7 Hz, C–^{13}CH$_3$), 46.92 (d, ^{5}J(H, P) = 9.0 Hz, N–^{13}CH$_2$), 20 signals from 121.4 to 148.6 ppm. – ^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$): δ = +0.24. – MS (EI, 70 eV): *m/z* = 384 (M+1, 28%), 383 (M, 100%), 355 (M+1 − Et, 23%), 354 (M − Et, 84%), 338 (M − NEt$_2$, 23%), 306 (M − Ph, 40%), 278 (M − Ph − C$_2$H$_4$, 69%). – C$_{26}$H$_{26}$NP (383.5): calcd. N 3.65, P 8.08; found N 3.81, P 8.13.

(8-Diethylamino-naphth-1-yl)-methyl-diphenyl-phosphonium iodide (**3a**) and *tetraphenylborate* (**3b**): Crystals of **3a** began to separate from a solution of 386 mg (1.01 mmol) of **2b** and 0.5 ml (8 mmol) of iodomethane in 4 ml of toluene within 3 min. After 30 d 527 mg (100%) of colorless **3a** was collected. M. p. 303 – 304 °C. – ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 0.65 (t, ^{3}J(H, H) = 7.2 Hz, 6H, C–C$^{1}H_3$), 2.28 (dq, ^{2}J(H^{A}, H^{B}) = 13.2 Hz, ^{3}J(H, H) = 7.1 Hz, 2H, N–C–$^{1}H^{A}$), 2.76 (dq, ^{2}J(H^{A}, H^{B}) = 13.4 Hz, ^{3}J(H, H) =

7.2 Hz, 2H, N$-$C$-{}^{1}H^{B}$), 3.12 (d, ${}^{2}J$(P, H) = 13.3 Hz, 3H, $P-$C${}^{1}H_{3}$), 7.41 – 8.26 (m, 16 H, arom. H).

340 mg (94%) of colorless **3b** precipitated from a solution of 263 mg (0.50 mmol) **3a** in 20 ml of methanol upon addition of 228 mg (0.67 mmol) of sodium tetraphenylborate dissolved in 10 ml of methanol and subsequent addition of 10 ml of water. Recrystallization from ethanol/acetone/water (45/15/10 ml) afforded 302 mg. M. p. 186 – 187 °C. – ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 0.62 (t, ${}^{3}J$(H, H) = 7.1 Hz, 6H, C$-$C${}^{1}H_{3}$), 2.21 (dq, ${}^{2}J$(H^{A}, H^{B}) = 13.5 Hz, ${}^{3}J$(H, H) = 7.2 Hz, 2H, N$-$C$-{}^{1}H^{A}$), 2.61 (d, ${}^{2}J$(P, H) = 13.5 Hz, 3H, $P-$C${}^{1}H_{3}$), 2.70 (dq, ${}^{2}J$(H^{A}, H^{B}) = 13.3 Hz, ${}^{3}J$(H, H) = 7.1 Hz, 2H, N$-$C$-{}^{1}H^{B}$), 6.78 – 8.25 (m, 36 H, arom. H). – ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$): δ = 8.99 (s, C$-{}^{13}C$H$_3$), 11.58 (d, ${}^{1}J$(P, C) = 65.8 Hz, P$-{}^{13}C$H$_3$), 46.28 (s, N$-{}^{13}C$H$_2$), 112.54 (d, ${}^{1}J$(P, C) = 92.8 Hz, C$_{ipso}$(Ph), 26 signals from 122.1 to 141.7 ppm, 147.35 (d, ${}^{3}J$(P, C) = 2.2 Hz, C(8)), 164.44 (q, ${}^{1}J$(B, C) = 49.3 Hz, C$_{ipso}$(BPh$_4^-$) – ^{31}P{^{1}H} NMR (81.0 MHz, CD$_2$Cl$_2$): δ = +24.46. – C$_{51}$H$_{49}$BNP (717.7): calcd. N 1.95, P 4.31; found N 2.04, P 4.31.

Crystal structure determination of (8-diethylamino-naphth-1-yl)-diphenyl-phosphine **(2b)**: C$_{26}$H$_{26}$NP, MG = 383.45 g/mol, transparent plate, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.6646 (3), b = 10.8802 (6), c = 21.972 (2) Å, V = 9657 (2) Å^3, T = 200 K, ρ_{calc} = 1.230 g·cm^{-3}, μ = 0.14 mm^{-1}, Z = 4, STOE Imaging Plate Diffraction System (IPDS), Mo-K$_\alpha$ (λ = 0.71073 Å), 200 K, 10871 measured reflections in the range of $3^\circ \leq 2\theta \leq 54^\circ$, 4315 independent reflections used for refinement, R_{int} = 0.0544). Structure solution was performed using SHELXS-86, structure refinement against F^2 using SHELXL-93. 271 refined parameters, R_1 for 3923 reflections with $I \geq 2\sigma(I)$ = 0.0373, wR_2 for all 4315 independent reflections = 0.0974, GoF 1.032, residual electron density: 0.20 / -0.23 Å^{-3}. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C$-$H hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using the riding model. The absolute structure was determined and is in agreement with the selected setting (Flack-x-parameter: 0.01 (8)).

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 206594. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 5Z, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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