peri-Interactions in Naphthalenes, 9 [1].
On Hypercoordination in Non-quaternary Phosphonium Salts and a Secondary Phosphine with the (8-Dimethylamino-naphth-1-yl) Substituent

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The ^{31}P NMR data of non-quaternary (8-dimethylamino-naphth-1-yl)phosphonium salts, with emphasis on the $^{1}J(^{31}P, ^{1}H)$ coupling constants, where scrutinized for their potential to yield information about N→P dative interactions. As for $\delta(^{29}Si)$ and $^{1}J(^{29}Si, ^{1}H)$ in the isosteric silanes, the data do not permit conclusions in favour of such interactions. $^{1}J(^{31}P, ^{1}H)$ of bis(8-dimethylamino-naphth-1-yl)phosphine in conjunction with the distances $d(N\cdots P)$ invalidates the basic assumption on which the claim of dative N→P/Si bonding in such phosphorus and silicon compounds rests, *viz.* that N$\cdots$P/Si distances of *ca.* 270 pm are evidence for P/Si-hypercoordination. No evidence for hydrogen bonds N$\cdots$H—P was found.

Key words: *peri*-Interactions in Naphthalenes, Hydrogeno-Phosphonium Salts and Phosphines

Introduction

The question whether N(donor) → P/Si(acceptor) interactions are operative in 8-dimethylamino-naphth-1-yl ("DAN") phosphorus compounds and silanes is presently subject to a controversial discussion (*cf.* Scheme 1) [2]. The key argument in favour of such "dative" interactions has been the fact that the experimentally found interatomic distances $d(N\cdots P/Si)$ (*ca.* 260–310 pm [3, 4]) are considerably shorter than the sum of the respective van der Waals radii, $\Sigma r(vdW_{N,P/Si}) = 325–345$ pm [5]. In the seminal paper on DAN-phosphines (**1**), N$\cdots$P distances of 280.5–285.3 pm have been claimed to represent crystallographic *proof* of Me$_2$N→P dative interaction (**1c**) [6]. In quaternary DAN-phosphonium salts (**2**) (in which the P atom should be more electrophilic than in DAN-phosphines), the claim of Me$_2$N→P dative interaction (**2c**) rests exclusively on $d(N\cdots P) = 282.6$ pm, again well below $\Sigma r(vdW_{N,P})$, in **5a** [7]. Whereas elsewhere hypercoordination at P causes considerable highfield shifts of the ^{31}P NMR signals [8], no such effect has been observed for **5a** and related salts [7, 9]; however, the feature did not serve to raise doubts about N→P da-

tive interaction, but was laconically discarded as being due to *"the specific geometry of the ligand"* [7].
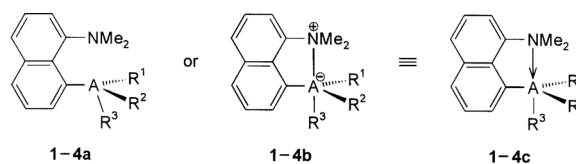
Scheme 1.

1: Phosphines; A = P, R^1 = lone pair

2: Quaternary phosphonium ions; A = P$^\oplus$, R^1, R^2, R^3 = alkyl and/or aryl

3: Non-quaternary phosphonium ions; A = P$^\oplus$, R^1, R^2, R^3 in part = alkyl and/or aryl, in part = H (in **2b**, **3b**, P uncharged)

4: Hydrogeno-silanes; A = Si, R^1, R^2, R^3 in part = H

It has been objected that the $d(N\cdots P/Si) < \Sigma r(vdW_{N,P/Si})$ argument is meaningless because the geometry of the naphthalene system does not permit the *peri*-bound atoms to reside at $\Sigma r(vdW)$ distance but rather enforces just those distances which have been experimentally observed [10–17]. Obviously, except for particularly favourable cases [14] the prob-

6 : A = PPh_2
7 : A = $P^{\oplus}HPh_2$ $X^{\ominus}$

	R^1	R^2	R^3	X		R^1	R^2
a	CH_2Ph	Ph	Ph	Br	a	H	NMe_2
b	H	DAN	Ph	TsO	b	H	$N^{\oplus}HMe_2$
c	H	DAN	Ph	Br	c	H	H
d	H	DAN	DAN	TsO	d	F	H
e	H	H	DAN	Br	e	Cl	H
f	H	H	DAN	$(3,5\text{-}(CF_3)_2C_6H_3)_4B$	f	Br	H
					g	I	H
					h	NMe_2	H

Scheme 2.

lem of N→P/Si dative interactions in DAN-P/Si compounds cannot be tackled by recourse to $d(\text{N}\cdots\text{P/Si})$; it is rather mandatory to find a property which responds *differently* to N→P dative interactions and their absence. We focussed our attention on the coupling constants $^1J(^{31}\text{P}, {}^1\text{H})$ of DAN(hydrogeno)phosphorus compounds ("DAN-P-H") which so far have not been the object of pertinent studies. On the one hand, if N→P dative interaction were possible in spite of the unfavourable geometry of the *peri*-naphthalene system [1], non-quaternary DAN-phosphonium salts, $R_{3-n}(\text{DAN})_n\text{P}^+\text{H X}^-$ (*cf.* **3**), should be particularly susceptible to such interactions: With the isosteric hydrogeno-silanes **4** they share decreased steric resistance against donor/acceptor interactions with respect to analogous quaternary phosphonium salts, but the P^+ centre should be a better electrophile than the P atom in the corresponding DAN-phosphines **1** and the Si atom in **4**. On the other hand, the secondary phosphine $(\text{DAN})_2\text{PH}$ would be the prime choice of a DAN-phosphorus compound with a nearly non-electrophilic P atom in which $d(\text{N}\cdots\text{P})$ would be shorter than $\Sigma r(\text{vdW}_{\text{N,P}})$ (possibly even particularly small because of the reduced steric congestion in the *peri* space, compared with tertiary DAN-phosphines such as $(\text{DAN})_2\text{PPh}$) and which yet might exhibit criteria of the absence of N→P dative interaction. In addition, both the salts **5** ($R^1 = \text{H}$) and $(\text{DAN})_2\text{PH}$ are of interest with respect to potential N···H—P hydrogen bonds. For obvious reasons, besides $^1J(^1\text{H}, {}^{31}\text{P})$, $\delta(^{31}\text{P})$ likewise deserves attention.

Non-quaternary phosphonium salts are available by protonation of phosphines. It was however doubtful whether protonation of DAN-phosphines would pro-

vide the envisaged salts (see Scheme 3). Dimethylaniline ($pK_a = 5.30$ [18]) is a much stronger base than triphenylphosphine ($pK_a = 2.73$ [19]). Accordingly, (4-dimethylamino-phenyl)diphenylphosphine had been found to be protonated at N [20]. On the other hand, the basicity of substituted triphenylphosphines is greatly enhanced by methoxy groups in *ortho* positions, *i. e.* in close proximity to the P atom (*e. g.* $pK_a = 3.33$ for $(2\text{-MeOC}_6\text{H}_4)\text{PPh}_2$, but 9.33 for $(2,6\text{-}(\text{MeO})_2\text{C}_6\text{H}_3)_3\text{P}$ and 11.02 for $(2,4,6\text{-}(\text{MeO})_3\text{C}_6\text{H}_2)_3\text{P}$ [21]). An analogous effect of the 8-Me_2N group might enable the P atom to override protonation at N. The occurrence or absence of $^1J(^{31}\text{P}, {}^1\text{H})$ coupling is a safe indicator of the site of protonation.
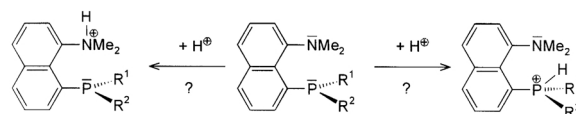
Scheme 3.

Results and Discussion

Tertiary DAN-phosphonium salts (5, $R^1 = \text{H}$)

Non-quaternary salts of DAN-phosphines have been prepared [6, 22, 23] and their solutions subjected to NMR spectroscopy [22, 23]. $^1J(^{31}\text{P}, {}^1\text{H})$ coupling indicated that protonation had occurred at the P atom [24] and was complete at 1:1 stoichiometry. Though both the signal positions and the values of the coupling constants may contain information about the formation of dative N→P bonds, neither $^1J(^{31}\text{P}, {}^1\text{H})$ nor $\delta(\text{R}^2\text{R}^3(\text{DAN})^{31}P^+\text{H})$ yields straightforward evidence. It was therefore indispensible to conduct comparative studies on other triarylphosphines. Many triarylphosphines which were useful for comparison are so weakly basic that complete protonation requires a substantial excess of acid. We therefore conducted our protonation studies in the NMR tubes by addition of increasing amounts of strong acids to CDCl_3 (occasionally CD_2Cl_2) solutions of the neutral bases and, for the sake of consistency, did so also in the case of the DAN-phosphines. With *p*-toluenesulfonic acid (TsOH), the stoichiometry could be monitored NMR-spectroscopically by integration ($\text{C}H_3$ of TsOH *vs.* N($\text{C}H_3)_2$ in DAN-phosphines). For a large excess of acid, a less precise determination of its amount was sufficient; trifluoroacetic acid (TFA) was used and its quantity determined by weight. Depending on its

amount, TFA gradually acquired the character of a protic cosolvent which may affect signal positions. The results are presented in Table 1.

The ^{31}P NMR signal positions $\delta(R_3P^+H)$ and the protonation shifts $\Delta\delta = \delta(R_3P^+H) - \delta(R_3P)$ depend on a variety of parameters. In tertiary *ortho*-substituted phenylphosphines the *ortho-effect* [12, 25] plays an important role. In naphth-1-yl phosphines the benzo anellation is equivalent to an *ortho*-substituent [12]. In the DAN-phosphines, this highfield shift effect is overcompensated by a downfield shift caused by the Me_2N group(s) so that DAN-phosphines absorb at somewhat lower field than Ph_3P [12]. In the series $(Me)(2\text{-}MeC_6H_4)_nPh_{3-n}P^+Br^-$ (n = 0–3), $\delta(^{31}P)$ is virtually constant [26]; hence, these *quaternary* salts are not subject to the *ortho*-effect [26]. Comparison of the $\delta(^{31}P)$ data of several salts $(R)Ph_2(DAN)P^+$ X^- and their 4-isomers (hence 8-unsubstituted) [9] discloses that in quaternary naphth-1-yl phosphonium salts neither the *ortho*-effect nor the *peri*-Me_2N effect is operative. This is corroborated by the series $(R)(PhCH_2)Ph_2P^+$ Br^- ($\delta(^{31}P)$: R = Ph: +23.5 [27]; α-$C_{10}H_7$: +22.45 [7]; DAN: +21.21 [9, 28], +22.12 [7, 29]). As a consequence the quaternization shift $\Delta\delta^Q = \delta(R_3P^+R') - \delta(R_3P)$ is far from constant, *viz.* unusually large for *ortho*-substituted triarylphosphines including naphth-1-yl phosphines and very small for tertiary DAN-phosphines.

Protonation experiments with the respective phosphines reveal that *tertiary* phosphonium salts behave differently (see Table 1). In the series $(2\text{-}R\text{-}C_6H_4)_nPh_{3-n}P$ (R = Me, n = 0–3), each additional *ortho*-R causes an almost constant highfield shift of $\Delta\delta \approx 8$ ppm [12]. The P-protonated species exhibit the phenomenon to almost the same extent, slightly increasing with increasing *n*. The naphth-1-yl phosphines $(\alpha\text{-}C_{10}H_7)_nPh_{3-n}P$ (n = 0–3) as well as their P-protonated derivatives show an almost identical behaviour, $\delta(R_3P)$ and $\delta(R_3P^+H)$ of $(\alpha\text{-}C_{10}H_7)_3P$ being very close to the respective values of $(2\text{-}Et\text{-}C_6H_4)_3P$.

Not surprisingly, **6a** is first protonated at the Me_2N group (**6a** → **6b**): Upon addition of 1 equivalent of TsOH, the ^1H NMR singlet of $N(CH_3)_2$ was shifted to lower field by $\Delta\delta(^1H) = +0.61$ ppm whereas $\delta(^{31}P)$ experienced a small downfield shift of $\Delta\delta(^{31}P) = +1.23$ ppm which may represent a substituent effect (replacement of the potential (+M)-substituent Me_2N by the (−I)-substituent $Me_2(H)N^+$ [30]). Addition of a second equivalent of TsOH affected neither $\delta(N\text{-}CH_3)$ nor $\delta(^{31}P)$. Further addition of acid gradually shifted

the ^{31}P signal to a final position of $\delta = +1.81$, similar to $\delta = +1.02$ of **7c**; the minute difference of $\Delta\delta = 0.8$ ppm does not warrant a comment but may be rationalized as due to a substituent effect exerted by the electronegative 4-$Me_2(H)N^+$ group upon the P atom. The ^1H resonance of N—CH_3 was shifted slightly to still lower field by another 0.12 ppm, possibly in consequence of a substituent effect ($Ph_2(H)P^+$ rather than Ph_2P) exerted upon the $Me_2(H)N^+$ group, though this may simply be a solvent effect caused by the addition of 146 mg TFA to 0.6 ml of $CDCl_3$. The N^+—H proton gave rise to a very broad signal at *ca.* 6.0 ppm upon addition of the first equivalent of TsOH; at higher acid concentrations a somewhat sharper signal was recorded whose position, however, was determined by the large excess of TFA.

In conclusion, Me_2N, being more basic than P, is already fully protonated by the first equivalent of acid. Only at substantially higher acid concentrations, the P atom is protonated, too. With 12 equivalents of acid, diprotonation is still a dynamic process which prevents $^1J(^{31}P, ^1H)$ coupling from being observed. The latter phenomenon occurred with some of the less basic substituted triarylphosphines, too.

Because of the close proximity, enhanced substituent effects may be envisaged for groups in the 8- (rather than 4-) position of tertiary naphth-1-yl phosphonium salts. Some insight into the effects of *peri*-substitution upon P-protonation was obtained from the series **6c – g**. Both the size (I > Br > Cl > F > H) and the electronegativity of R^1 (H < I < Br < Cl < F [31]) may have an impact. Electron donation Hal→P seems unlikely [16].

In the series of the phosphines, the highfield position of the ^{31}P signal due to the *ortho-effect* (**6c**: $\delta = -13.33$) is only slightly affected by introduction of the most bulky substituent, I, without much change in the electronegativity ($\Delta\delta(\mathbf{6g/c}) = +1.35$ ppm). *peri*-Br, Cl and F cause greater downfield shifts, though $\Delta\delta$ decreases regularly ($\Delta\delta(\mathbf{6f/g}) = +6.10$, $\Delta\delta(\mathbf{6e/f}) = +3.47$, $\Delta\delta(\mathbf{6d/e}) = +2.86$ ppm). For $R^1 = Me_2N$, the ^{31}P signal position, $\delta = +0.54$ (*i. e.* at the low field end of the series, $\Delta\delta(\mathbf{6h/c}) = +13.87$), correlates neither with the electronegativity (Br < Cl = N < F [31]) nor with the estimated size (*cf.*, *e. g.*, *r*(vdW): H < F < N < Cl < Br < I [5]), but certainly does not indicate N→P donation for which a signal position at particularly *high* field would be anticipated. Qualitatively, the tertiary phosphonium salts **7** follow the same trends though $\Delta\delta(\mathbf{7g/c}) = +3.29$ ppm is larger and $\Delta\delta(\mathbf{7f/g}) =$

Table 1. Protonation studies with tertiary and secondary phosphines (^{31}P NMR, 81.0 MHz; a = ^{1}H-decoupled, b = ^{1}H-coupled; solvent: CDCl$_3$; acid: A = 4-Me-C$_6$H$_4$SO$_3$H, B = F$_3$C-COOH, R^{1,2}: Ph = phenyl, Np = naphth-1-yl).

Phosphine: R^1_nR$^2_{3-n}$P			Acid	^{1}H	^{31}P NMR	^1J(P, H)	Protonation shift $\Delta\delta$	Notes
n	R^1	R^2	(equiv.)	(a/b)	δ[ppm]	[Hz]	[ppm]	
3	Ph	—	(0)	a	−4.49			
			A (1.08)	a	−1.60			
			A (1.08)	b	+5.65	467	+10.14	1
			+B (4.86)					
1	2-Me-C$_6$H$_4$	Ph	(0)	a	−12.47			2
			B (5.22)	b	+0.36		+12.83	
2	2-Me-C$_6$H$_4$	Ph	(0)	a	−20.38			
			B (5.82)	b	−6.12	486	+14.26	3
3	2-Me-C$_6$H$_4$	—	(0)	b	−28.91			4
			B (5.25)	b	−13.26	490	+15.65	
			B (5.97)	b	−13.26	474	+15.65	
3	2-Et-C$_6$H$_4$	—	(0)	b	−33.76			5
			B (6.56)	b	−15.24	492	+18.52	6
1	2,6-F$_2$C$_6$H$_3$	Ph	(0)	a	−27.35			7
			B (2.44)	a	−19.30			8
			B (2.44)	b	−19.21			9
			B (7.31)	a	−12.66			10
			B (7.31)	b	−12.67		+14.68	11
3	2-MeO-C$_6$H$_4$	—	(0)	b	−38.82			12
			B (1.02)	b	−24.01			13
			B (6.14)	b	−18.00	547	+20.82	14
3	2-MeO,5-MeC$_6$H$_3$	—	(0)	a	−38.07			
			B (1.98)	a	−18.93			
			B (1.98)	b	*ca.* −19.22	*ca.* 270		15
			B (11.87)	b	−19.33	546		16
1	Np (**6c**)	Ph	(0)	a	−13.33			
			A (1.30)	a	−7.88			
			A (1.30)	b	+1.02	512	+14.35	
			+B (7.20)					17
2	Np	Ph	(0)	a	−22.41			
			A (1.02)	a	−17.28			
			A (1.02)	b	−6.06	497	+16.35	17
			+B (11.26)					
3	Np	—	(0)	a	−32.27			
			A (1.02)	b	−26.6 *to* −28.5			18
			A (1.02)	b	−14.35	487	+17.92	19
			+B (7.70)					
1	2-Me-C$_{10}$H$_6$	Ph	(0)	a	−19.87			20
			B (7.15)	b	−9.76	501	+10.11	21, 22
1	8-I-C$_{10}$H$_6$ (**6g**)	Ph	(0)	a	−11.98			
			B (9.42)	b	+4.33	523	+16.31	21, 22
1	8-Br-C$_{10}$H$_6$ (**6f**)	Ph	(0)	a	−5.88			
			B (8.32)	b	+9.36	533	+15.24	22, 23
1	8-Cl-C$_{10}$H$_6$ ((**6e**)	Ph	(0)	a	−2.41			
			B (8.25)	b	+11.60	539	+14.01	22, 24
1	8-F-C$_{10}$H$_6$ (**6d**)	Ph	(0)	a	*d*, +0.45			25
			B (8.04)	a	*d*, +11.65		+11.20	26
			B (8.04)	b	*d*, +11.65	531		22, 27
1	2-F-C$_{10}$H$_6$	Ph	(0)	a	*d*, −25.08			28
			B (2.22)	a	*d*, −16.47			29
			B (2.22)	b	*d*, −16.49			30
			B (6.65)	a	*d*, −12.58		+12.50	31
			B (6.65)	b	−12.57			32

+5.03, $\Delta\delta$(**7e/f**) = +2.31, $\Delta\delta$(**7d/e**) = 0.0 ppm are somewhat smaller than in the phosphine series. For **7h**, δ = +2.94 ppm, a value close to δ(**7c**) = +1.02, suggests that no *peri*-Me$_2$N effect is operative. The presence of the *peri*-Me$_2$N effect in the phosphine and its

absence in the tertiary phosphonium salt explains the very small protonation shift, $\Delta\delta$ = +2.40 ppm. δ(^{1}H, N—CH_3) = 2.27 of the phosphine is virtually inert towards addition of even large amounts of acid: Protonation at P evidently prevents the creation of a second

Table 1 (continued).

Phosphine: $R_n^1 R_{3-n}^2 P$			Acid	^{1}H	^{31}P NMR	^1J(P, H)	Protonation shift $\Delta\delta$	Notes
n	R^1	R^2	(equiv.)	(a/b)	δ[ppm]	[Hz]	[ppm]	
1	4-Me$_2$N-C$_{10}$H$_6$	Ph	(0)	a	−13.98			33
	(**6a**)		A (1.01)	a	−12.75			34
			A (2.00)	a	−12.45			35
			A (2.00) +B (2.53)	a	−7.60			
			A (2.00) +B (5.06)	a	−1.49			
			A (2.00) +B (7.60)	a	+1.24			
			A (2.00) +B (10.12)	a	+1.82			
			A (2.00) +B (12.65)	b	+1.81	—	+15.79	36
1	8-Me$_2$N-C$_{10}$H$_6$	Ph	(0)	a	+0.54			37
	("DAN") (**6h**)		A (0.91)	a,b	+1.66			38
			A (1.01)	b	+1.79			39
			A (2.28)	b	+2.94	504	+2.40	40
2	8-Me$_2$N-C$_{10}$H$_6$	Ph	(0)	a	+4.47			41
	("DAN")		A (1.03)	b	+9.70	640		42, 43
			A (1.08)	b	+8.45	653		42, 44
			B (9.67)	b	+10.87	628	+6.40	42, 45
3	8-Me$_2$N-C$_{10}$H$_6$	—	(0)	a	+5.97			46
	("DAN")		B (9.46)	b	+13.63	691	+7.66	47
2	8-Me$_2$N-C$_{10}$H$_6$	H	(0)	b	d, −22.85	208		48
	("DAN")		A (0.97)	a	−15.84		+7.01	49
			A (1.45)	b	t, −15.93	590	+6.92	50, 51
			A (2.04)	b	t, −16.94	585	+5.91	50, 52
			B (8.77)	b	tt, −19.64	561		53

Notes: [The notes refer to ^{31}P NMR spectra unless otherwise stated.] (1) Doublet of two very broad signals. – Lit.: ^1J(^{31}P, ^{1}H) = 480 Hz [26], 506 Hz [47].– (2) One very broad signal; protonation presumably not complete. –^1J(^{31}P, ^{1}H) = 514 Hz [26]. – (3) Two fairly broad signals. – ^1J(^{31}P, ^{1}H) = 508 Hz [26]. – (4) One fairly sharp signal; no ^3J(^{31}P, ^{1}H) visible. – (2-Me-C$_6$H$_4$)$_3$P$^+$H: ^1J(^{31}P, ^{1}H) = 515 Hz [26]. – (5) No ^3J(^{31}P, ^{1}H) visible. – (6) Doublet; no ^3J(^{31}P, ^{1}H) visible. – (7) Triplet; ^3J(^{31}P, ^{19}F) = 42 Hz. – (8) Triplet; ^3J(^{31}P, ^{19}F) = 24 Hz. – (9) One signal; fine structure poorly resolved. – (10) Triplet; ^3J(^{31}P, ^{19}F) = 10 Hz. – (11) One signal; neither ^1J(^{31}P, ^{1}H) nor ^3J(^{31}P, ^{19}F) visible. – (12) One signal with well resolved fine structure, presumably ^5J(^{31}P, OC^{1}H$_3$) = 4.5 Hz. – (13) One ^{31}P signal, somewhat broader; no fine structure. – (14) Two signals with fine structure ^5J = 4.7 Hz. – ^1J(^{31}P, ^{1}H) = 542 Hz [26]. – (15) Incipient, but still unstable protonation. – (16) Nine peaks each; ^5J(^{31}P, ^{1}H) = 9.3 Hz; no ^3J(^{31}P, ^{1}H) coupling! – (17) Doublet without fine structure. – (18) Complicated signals. – (19) Two signals, each as a doublet; $\Delta\delta$ = 12 Hz. – (20) ^{1}H NMR (200.1 MHz): ^4J(^{1}H$_{peri}$, ^{31}P) = 4.1 Hz. – (21) Doublet of fairly narrow signals. – (22) No further coupling visible. – (23) Doublet of broadened signals. – (24) Doublet of somewhat broadened signals. – (25) ^4J(^{31}P, ^{19}F) = 194 Hz. – (26) ^4J(^{31}P, ^{19}F) = 44 Hz. – (27) Two fairly broad signals. – (28) ^3J(^{31}P, ^{19}F) = 5.0 Hz. – (29) ^3J(^{31}P, ^{19}F) = 11.0 Hz. – (30) ^3J(^{31}P, ^{19}F) = 10.5 Hz. – (31) ^3J(^{31}P, ^{19}F) = 17.3 Hz. – (32) One broad signal: No stable protonation. – (33) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.86. – (34) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 3.47. – (35) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 3.42. – (36) ^{31}P NMR: Somewhat broadened s; ^{1}H NMR (200.1 MHz): N-CH_3 δ = 3.59. Protonation shift Me$_2$N → Me$_2$N$^+$H: +0.61. – (37) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.27. – (38) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.41. – (39) ^{31}P NMR: Broadened s; ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.40. – (40) ^{31}P NMR: Broad d; ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.33. A (2.28) + B (2.02): ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.30; A (2.28) + B (5.32): ^{1}H NMR (200.1 MHz): N-CH_3 δ 2.33. – (41) ^{1}H NMR (200.1 MHz): N-CH_3 δ 1.57, 1.69, 2.55, 2.80 (broad signals). – (42) ^{31}P NMR: d; each signal is a well resolved quintuplet. – (43) In CD$_2$Cl$_2$; ^3J(^{31}P, ^{1}H) = 16.9 Hz; ^{1}H NMR (500.1 MHz): N-CH_3 δ = 1.53, 1.68, 2.65, 2.92 (broadened signals). – (44) ^3J(^{31}P, ^{1}H) = 16.1 Hz. – (45) ^3J(^{31}P, ^{1}H) = 16.0 Hz; ^{1}H NMR (200.1 MHz): N-CH_3 δ = 1.52, 1.67, 2.62, 2.90 (sharp signals). – (46) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 1.45, 2.70 (sharp signals). – (47) Doublet of quartets; ^3J(^{31}P, ^{1}H) = 17.4 Hz. ^{1}H NMR (200.1 MHz): N-CH_3 δ = 1.47, 2.79 (sharp signals). – (48) Doublet. ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.35 (broad signal), 2.63 (sharp signal), P-H δ 5.84, d, ^1J(^{1}H, ^{31}P) = 208 Hz. – (49) ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.75 (broad signal); P-H (?): δ = 4.94 (br. s). – (50) ^{31}P NMR: ^1J(^{31}P, ^{1}H) t; central signal: broadened s. – (51) Lateral signals: t (poorly resolved). – (52) Lateral signals: t; ^3J(^{31}P, ^{1}H) = 19.9 Hz. ^{1}H NMR (200.1 MHz): N-CH_3: broad absorption, *ca.* 2.3 – 2.7; P-H: no signals in the region *ca.* 5.3 – 6.4. δ = 8.69 (br. s) may be an averaged absorption of P-H and TsOH. – (53) tt, ^3J(^{31}P, ^{1}H) = 19.7 Hz. ^{1}H NMR (200.1 MHz): N-CH_3 δ = 2.27, 2.74 (moderately broadened signals); P-H: no signals in the region *ca.* 5.3 – 6.4. δ 9.59 (br. s) should be mainly due to F$_3$C-COOH.

positive charge within the small *peri* space. The feature is paralleled by the *proton sponge*[TM], DAN-NMe$_2$, of which no dication is available either [32]. Similarly, DAN-N$^+$Me$_3$ BF$_4^-$, though kinetically protonated at the Me$_2$N group, is preferentially protonated at C(7) by thermodynamic control [33]. However, the virtually total insensitivity of the N-CH_3 signal towards P-protonation in the immediate vicinity may be taken as evidence that the protonation is entirely a process at the P atom, *i. e.* that the Me$_2$N group is not engaged in a [N$\cdots$H$\cdots$P]$^+$ hydrogen bond. On the other hand, the ^{31}P signal is well within the range of tertiary phosphonium salts so that again no N→P donation is indicated either. Complete P-protonation already by 2.3 equivalents of acid indicates that Ph$_2$(DAN)P (**6h**) is much more basic than, *e. g.*, Ph$_3$P and the other phosphines Ph$_2$(8-R^1-C$_{10}$H$_6$)P (**6c−g**). The influence of the 8-Me$_2$N group is obvious, but provides no evidence for N→P donation, because phosphines are known in which the P atom owes its even higher basicity to the proximity of comparable substituents in spite of their poor σ-donicity and the unavailability of the required number of suitable orbitals at P [21] (*vide supra*).

The additive effect of up to six *ortho*-methoxy groups upon the basicity of triphenylphosphines [21] is paralleled by the bis(DAN)phosphine Ph(DAN)$_2$P which is even more basic than **6h**: Already the first equivalent of TsOH achieves complete P-protonation. Again the protonation shift is small ($\Delta\delta = +3.9$ ppm); a slight enhancement by 2.5 ppm upon addition of 9.7 equivalents of TFA may be caused by the change of the "solvent" (*cf.* the solvent effect from CDCl$_3$ to CD$_2$Cl$_2$: $\Delta\delta = \delta($**5b** / CD$_2$Cl$_2) - \delta($**5b** / CDCl$_3) = 1.25$ ppm). In the 200 MHz ^{1}H NMR spectrum of Ph(DAN)$_2$P, the Me$_2$N region consists of four broadened singlets at 1.57, 1.69, 2.55 and 2.80 ppm (lit. [4]: 1.55, 1.72, 2.52, 2.75, 250 MHz, room temperature, C$_6$D$_6$). The pattern resembles those in the bis(DAN)silanes **4** (R^1 = DAN, R^2 = H, R^3 = F, OMe, Me, Ph) (*e. g.*, R^3 = Ph: δ = 0.83/1.18, 1.47/1.69, 1.96/2.30, 2.42/2.35 (two isomers)) [34] and in the carbinol (HO)(DAN)$_2$CH (δ = 1.56, 2.42, 2.91, 3.06) [10] which have been ascribed to hindered rotation around the C(1)—Si/C and the C(8)—N bonds of the naphthalene system [10, 11]. P-protonation has little effect (1 equiv. of TsOH: δ = 1.53, 1.68, 2.66, 2.93; 9.7 equiv. TFA: δ = 1.52, 1.67, 2.62, 2.90); the singlets, still broadened in the 500 MHz spectrum of **5b**, are sharp in the 200 MHz spectrum obtained in pres-

ence of 9.7 equiv. of TFA. A NOESY spectrum of **5b** revealed the same pairwise correlation as for the carbinol [10], *i. e.* signals 1 and 4 originating from one pair of Me groups and signals 2 and 3 from the other pair. The signal separations of the "outer" signals are similar, while those of the "inner" signals are rather different (carbinol: 1/4: 450 Hz (300 MHz) ($\equiv$ 300 Hz (200 MHz)); 2/3: 146 Hz (300 MHz) ($\equiv$ 97 Hz (200 MHz)) [10]; **5b**: 1/4: 698 Hz (500 MHz) ($\equiv$ 279 Hz (200 MHz)); 2/3: 489 Hz (500 MHz) ($\equiv$ 196 Hz (200 MHz)); Ph(DAN)$_2$P + 9.7 equiv. TFA (200 MHz): 1/4: 276 Hz; 1/3: 190 Hz). Likewise, the proton-decoupled 126 MHz ^{13}C NMR spectrum of **5b** contained 4 N—CH_3 signals at 43.7, 46.4, 47.3 and 49.5 ppm (for comparison: 2 signals for the diastereotopic geminal CH_3 groups of both enantiotopic Me$_2$N groups of the carbinol at 75 MHz, δ = 46.9 and 47.3 [10]). In conclusion, replacement of the (HO)C segment in (HO)(DAN)$_2$CH by PhP$^+$ changes very little; protonation of Ph(DAN)$_2$P takes place at P and precludes further protonation at the Me$_2$N groups. Though still potential σ-donors, they establish no N→P$^+$ bonds. The conclusion is in accord with the crystal structure of **5c** [22, 35]: The distances d(N$\cdots$P) exceed the "natural" *peri* distance of 250 pm [11 – 14, 17] by 20/24 pm. Though the bond angles N—C(8)—C(9), 116.6 and 116.8°, fall short of 120°, the splay angles, +7.0 and +4.7°, indicate substantial intersubstituent repulsion [36]. As usual, the main burden of the distortion of the C$_{10}$ skeletons is carried by the angle C(1)—C(9)—C(8). **5c** thus complies perfectly with all criteria of *peri*-disubstituted naphthalenes with repulsive interaction between the substituents.

Replacement of the phenyl group in Ph(DAN)$_2$P by a third DAN group causes a slight ^{31}P NMR downfield shift of $\Delta\delta = +1.5$ ppm. After addition of *ca.* 9.5 equiv. of TFA to either phosphine, the same substitution process amounts to 5.25 ppm; *i. e.* the protonation shift is larger (+7.66 ppm), but still small. $^1J(^{31}$P, ^{1}H) coupling indicates complete P-protonation. The 200 MHz ^{1}H spectra exhibit two Me$_2$N singlets, δ = 1.46 and 2.70 ($\Delta\delta$ = 248 Hz) which are virtually inert towards acidification with 9.5 equiv. of TFA (δ = 1.47 and 2.79, $\Delta\delta$ = 265 Hz). Thus protonation is again restricted to P, and the Me$_2$N groups make no use of the improved conditions for N→P$^+$ bonding. Crystal structure determinations [23] revealed for (DAN)$_3$P C—P—C angles typical for tertiary phosphines (99.8°, average) which are enlarged by 7.0° upon protonation. A slight decrease of d(N$\cdots$P) (from 284.4 to 281.3 pm, averages)

is counterbalanced by a slight increase of the splay angles (from $+6.7°$ to $+8.4°$, averages); the phosphine and the cation then resort in a slightly different manner to in-plane and out-of-plane distortion for relief from steric congestion, but both exhibit the criteria of repulsion.

$^1J(^{31}P, ^1H)$ coupling constants

The $J(^{31}P, ^1H)$ coupling constants were obtained from the proton-coupled ^{31}P NMR spectra. In some cases they were counterchecked in the ^1H NMR spectra. Some phosphines used for comparison were so weakly basic that complete protonation could not be achieved or, though complete, remained kinetically unstable so that no coupling was observed. In some cases, the proton exchange with excess TFA was slowed down sufficiently so that $^1J(^{31}P, ^1H)$ became measurable, but the signals remained broad. In most cases, however, including the DAN-phosphines, nicely resolved spectra were obtained some of which exhibited additional $J(^{31}P, ^1H)$ couplings. In the spectra of the protonated phosphines containing F, $J(^{31}P, ^{19}F)$ was well resolved. The results are summarized in Table 1.

It had been claimed that in DAN-silanes $R^1R^2(DAN)SiH$ (**4**, $R^3 = H$) $^1J(^{29}Si, ^1H)$ is a reliable feature for discriminating hyper- from tetracoordinate Si [34]. However, closer inspection of the data had revealed that the respective ranges of $^1J(^{29}Si, ^1H)$ overlap and that therefore no unambiguous information is available [10]. Similarly, the $^1J(^{31}P, ^1H)$ ranges for different oxidation states of P—H compounds are known to overlap considerably though there is a general increase with increasing coordination number [37]. $^1J(^{31}P, ^1H) = 504$ Hz of **7h** is just in the centre of the $^1J(^{31}P, ^1H)$ range of protonated phosphines and thus in full accord with the non-dative phosphonium formula (*cf.* **3a**). In the alternative formulae **3b,c**, the cation would have a phosphorane structure with three P—C bonds, one P—N$^+$ bond and one P—H bond (C$_3$N$^+$PH type) [38]. Unfortunately, no authentic compounds of this type are available for comparison. Cyclic hydrogeno-phosphoranes of the types N$_2$O$_2$PH, NO$_3$PH and O$_4$PH exhibit $^1J(^{31}P, ^1H)$ coupling constants of 732–829, 779–905 and 804–918 Hz, respectively [39], hence much larger values. However, this strong coupling is partially caused by the high electronegativity of the atoms attached to P [37]; a C$_4$PH type phosphorane exhibited only $^1J(^{31}P, ^1H) = 482$ Hz [40], hence within the

range of protonated tertiary phosphines, R$_3$P$^+$H [39]. For a C$_3$N$^+$PH system a $^1J(^{31}P, ^1H)$ value somewhere between 482 Hz and the 732–918 Hz range would be anticipated. Electronically, a C$_3$OPH system prepared by Ross and Martin [41] having O (Pauling electronegativity 3.5 [31]) instead of N$^+$ (Pauling electronegativity *ca.* 3.3 [42]) would appear to come closest to the phosphorane form (**3b,c**) of Ph$_2$(DAN)P$^+$H. However, the compound does not qualify for comparison, because the hydrogen atom has been found to be in the unusual apical rather than in the normal equatorial position, a fact which is believed to account for the exceptionally small value $^1J(^{31}P, ^1H) = 266$ Hz [41], considerably below the R$_3$P$^+$H range [39]. Alternatively, the effect of charge on the coordinated N atom could be taken into account by replacement of one P—C bond by another P—N bond or by a P—O bond, but C$_2$N$_2$PH or C$_2$NOPH phosphoranes seem to be unknown either [39]. For Me$_2$F$_2$PH, hence a C$_2$F$_2$PH system, $^1J(^{31}P, ^1H) = 733$ has been reported [43]. Thus, while dative N→P interaction cannot be strictly ruled out, $^1J(^{31}P, ^1H)$ of **7h** is fully compatible with tetracoordinate P$^+$.

The $^1J(^{31}P, ^1H)$ coupling constants of **5b** and **5d** are much larger and no longer within the range covered by the reference material of R$_3$P$^+$H structures. In **5b**, two N→P interactions would render the P atom hexacoordinate (C$_3$N$_2$PH system). $^1J(^{31}P, ^1H)$ of authentic P—H phosphates covers the same range as for hydrogeno-phosphoranes [39]. The closest analogy (a C$_2$F$_3$PH system) is provided by the (CF$_3$)$_2$F$_3$PH$^-$ anion, $^1J(^{31}P, ^1H) = 622$ Hz [44]. Several CO$_4$PH phosphate systems exhibited $^1J(^{31}P, ^1H)$ values from 620 to 716 Hz [45, 46]. Though $^1J(^{31}P, ^1H) = 628–640$ Hz of Ph(DAN)$_2$P$^+$H fits well into this frame, N→P$^+$ interaction is not an attractive rationalization in view of the "*typical phosphonium*" $^1J(^{31}P, ^1H)$ value of **7h**: Since, as a general rule, phosphorus attains pentacoordination more easily than hexacoordination, and heptacoordination not at all, it can hardly be assumed that while there is no such interaction in **7h**, two and three Me$_2$N groups jointly engage in dative N→P bonds and render the P atom hexa- and even hepta-coordinate. Conceivably, the increase of $^1J(^{31}P, ^1H)$ in **5b** and **5d** could be caused by the geometrically enforced proximity of the electronegative Me$_2$N groups. For covalently bound electronegative atoms the corresponding effect has been observed in hydrogeno-phosphonium salts as well as in hydrogeno-bis(1,2-phenylenedioxy)phosphates

(e. g., $(MeO)_nPh_{3-n}P^+H$, $n/^1J$: 0/506, 1/553, 2/666, 3/830 Hz; for comparison: Ph_2ClP^+H 561, $PhCl_2P^+H$ 653 Hz [47]; $(C_6H_4O_2)_2(R)P^-H$, $R/^1J$: Me/620–624, Ph/642–646, C_6F_5/716, MeO/800 Hz [46]).

Other couplings

$^3J(^{31}P, ^1H)$ couplings are ubiquitous in organophosphorus compounds [48]. Therefore, coupling of ^{31}P with the *ortho*-protons of Ph groups and with the 2-protons of naphth-1-yl groups may be expected. In most cases, this was not observed in the ^{31}P spectra. Presumably, two reasons play a role. First, $^3J(^{31}P, ^1H)$ coupling tends to be smaller in phosphines than in phosphonium salts. ^3J will therefore be less easily detected as long as protonation is incomplete. Second, the less basic phosphines yielded broadened signals upon acidification in which no fine structure was resolved. Due to their high basicity, the DAN-phosphines behaved differently. Whereas **6h** still gave a broadened ^{31}P NMR singlet upon addition of 1 equiv. of TsOH and a broad doublet (^1J = 504 Hz) with 2.3 equiv., **5b** gave a ^1J doublet each signal of which was a well resolved quintuplet with J = 16 Hz. Though ^1J was somewhat smaller in the presence of 9.7 equiv. of TFA (presumably attributable to a solvent effect), the quintuplets persisted unchanged. The obvious explanation is ^3J coupling with the two protons 2-H of the DAN groups and the two protons 2-, 6-H of the Ph group. Correspondingly, the spectrum of $(DAN)_3P$ + 9.5 equiv. of TFA exhibited a doublet (^1J = 691 Hz) of quartets, ^3J = 17.4 Hz (three protons 2-H). For $^3J(^{31}P, ^1H)$ and long range $^{31}P, ^1H$ couplings [49] in the triphenylphosphine derivatives *cf.* Table 1.

Comparison of the $^{31}P, ^{19}F$ couplings in $Ph_2(8\text{-F-}C_{10}H_6)P$, its 2-F-$C_{10}H_6$ isomer and their P-protonated derivatives (Table 1) reveals through space coupling between the *peri* substituents [50] and the decisive role of the lone pair at the P atom for it. To be sure, through-space coupling, according to presently accepted theories [51], has no bearing on *bonding* interactions.

Bis(8-dimethylamino-naphth-1-yl)phosphine ((DAN)₂PH)

Steric opposition against *peri* donor→acceptor interaction should be further reduced in the secondary phosphine $(DAN)_2PH$ and its P-protonated derivative, $(DAN)_2P^+H_2$. Generally, secondary phosphines are much less basic than tertiary phosphines [19] so that at the first glimpse P-protonation in the presence of

Me_2N groups would seem impossible. However, the preparation of **5e,f** has been reported [22]. The bromide **5e** has been described as a crystalline compound which was highly unstable both in solution and in air [52]. Instability was also assumed for solutions of the tetraarylborate **5f** for which no melting point was recorded. The ^{31}P NMR spectra of both salts exhibited three equidistant signals at distances of $\Delta\delta$ = 5.84 and 5.58 ppm, respectively, which were interpreted as triplets with $^1J(^{31}P, ^1H)$ = 590 and 564 Hz, respectively. These numbers fit well into the range of $^1J(^{31}P, ^1H)$ of *tertiary* phosphonium salts (*vide supra*), and the multiplicity is in accord with P-protonation. However, some details were bewildering. The same coupling constant was identified in the ^1H NMR spectrum of **5e**, but the respective signals, δ = 8.85, were likewise described as a *triplet* [53]. $\delta(^{31}P)$ was given as −6.3 (in $CDCl_3$) [53] as well as −6.8 (solvent not given; possibly CD_2Cl_2 for adequate comparison with $\delta(CD_2Cl_2)$ of **5f**) [54] whereas **5f** was reported to resonate at δ = − 16.25 (in CD_2Cl_2) [53, 54]. The difference of *ca.* 10 ppm was rated as "*slightly different according to the anion... This difference may result from an interaction between the anion and the phosphorus atom, an interaction which should be more important in [the bromide] than in [the tetraarylborate]*" [54].

In the course of our previous studies on ion pair association of quaternary phosphonium halides and tetraphenylborates [9, 55] we had found impressive highfield shifts of ^1H NMR signals which were caused by the formation of contact ion pairs (in fact, *penetrated ion pairs* [56]) between R_4P^+ and Ph_4B^-. However, exploratory studies of the ^{31}P NMR signal positions revealed that no comparable effect exists in ^{31}P NMR spectroscopy [57]. In our opinion, an anion effect of $\Delta\delta$ = *ca.* 10 ppm is impossible. We refrain from an attempt to rationalize the published data and preferred to conduct an independent study.

Synthesis and structure of (DAN)₂PH

$(DAN)_2PH$ had previously been synthesized via a conventional route [22]. We obtained it in an abortive attempt to prepare $(Me_2CH)(DAN)_2P$ from isopropylmagnesium bromide and chloro-bis(8-dimethylamino-naphth-1-yl) phosphine. Presumably the first step was a halogen/metal exchange to give Me_2CHCl and $(DAN)_2PMgBr$ which in the work-up hydrolyzed to $(DAN)_2PH$ (Scheme 4). As not all of the properties
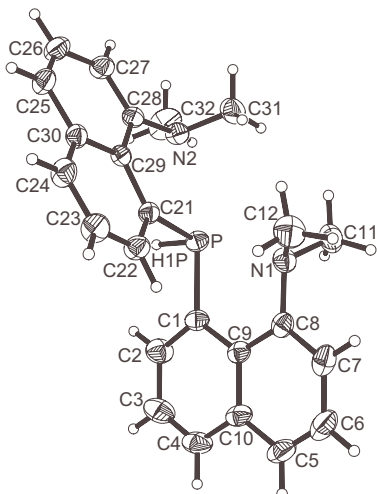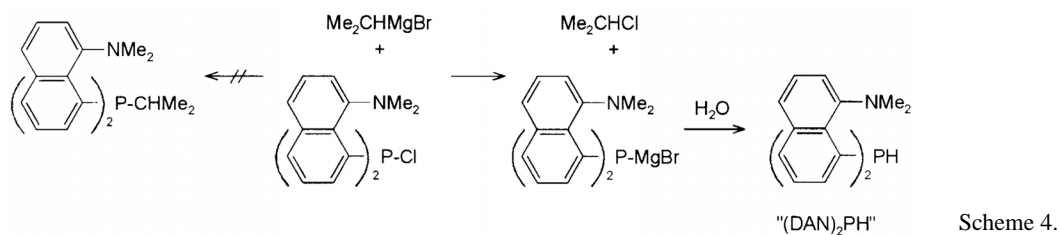
Scheme 4.

Fig. 1. Crystal structure of (DAN)$_2$PH with labelling and displacement parameters drawn at the 50% probability level.

agreed with the published data (*vide infra*), we performed a thorough characterization including an X-ray structure determination.

We obtained (DAN)$_2$PH as yellow, not air-sensitive crystals [58] which gradually liquefy between 140 and 150 °C [59] (118 – 119 °C [60]) and which turned out to be well suited for a single crystal structure determination (Fig. 1).

The angle C(1)—P—C(21) (102.5°) is almost identical with the corresponding angle in Ph(DAN)$_2$P (101.4°) [4] and the C—P—C angles in Ph$_3$P (102.1, 103.3, 103.6° [61]), whereas the angles C(1)—P—H and C(21)—P—H (93.0 and 95.4°) are smaller than the angles C(1)^I—P—C$_{Ph}$ and C(1)^{II}—P—C$_{Ph}$ in the tertiary phosphine (100.4 and 101.7° [4]). The difference can be ascribed to decreased steric hindrance between DAN and H. The N···P distances (d(N(1)···P) = 279.1, d(N(2)···P) = 270.2 pm) are longer than the "natural" *peri* distance of 250 pm [11 – 14, 17] by 29 and 20 pm, respectively. In the tertiary phosphine,

the two N···P distances (278.0 and 279.2 pm) are almost equal. In (DAN)$_2$PH one of them (d(N(1)···P) = 279.1 pm) is identical with the longer one, but the other one is 9 pm shorter. The same phenomenon, though even more pronounced, has been reported for the structurally related silane (DAN)$_2$SiH$_2$ (**4**, R^1 = DAN, R^2, R^3 = H) (d(N···Si) = 280.0 and 261.0 pm) [62]). As no reasons for the difference on the molecular level are obvious, the phenomenon provides a *caveat* towards interpreting differences of such magnitude in terms of bonding *etc*. d(N(1)···P) is close to that in bis(2,2'-biphenylylene)(DAN) phosphorane (281.0 pm) which according to Day and Holmes "*is not indicative of a bonding interaction of any appreciable magnitude*" [63]. Concomitantly with the increased N···P distances, the non-bonding intra-skeleton distances d(C(1/21)···C(8/28)) = 253.3, 253.2 pm are longer than the "natural" *peri* distance of 247 pm [10, 14, 16], while d(C(4/24)···C(5/25)) = 245.1, 245.4 pm is slightly shorter.

Within each DAN group, the bay angles exhibit the wide-spread phenomenon that both the angle P—C(1/21)—C(9/29) (124.3/122.3°) and the angle C(1/21)—C(9/29)—C(8/28) (124.0/123.7°) are larger than 120° whereas the angle N(1/2)—C(8/28)—C(9/29) is slightly smaller (118.3/117.4°). The results are positive splay angles of the *peri* bonds of +6.6 and +3.4°, correlating with the longer and the shorter N···P distance, respectively. In the afore-mentioned DAN-phosphorane, the corresponding data are very similar (P—C(1)—C(9) 123.2°, C(1)—C(9)—C(8) 123.3°, N—C(8)—C(9) 116.7°, splay angle +3.2° [63]). The resemblance suggests a common cause of the observed phenomena. While very different in respect of bonding at the P atom (*pseudo*-tetrahedral *vs.* pentacoordinate-trigonal bipyramidal), both compounds share the steric constraints in the *peri* space so that the bay angles and d(N···P) are likely to be conditioned by the common steric situation. Formal engagement of the P-lone pair in a P-C$_{phenyl}$ bond ((DAN)$_2$PH → **5c**) causes the expected enlargement of the C(1)$_{DAN}$—P—C(1')$_{DAN}$

angle from 102.5° to 108.4°, but otherwise has almost no effect [64]. Except for a slightly different balance of the burden of angle enlargements among the bay angles no effect of the structural change is apparent.

In (DAN)$_2$PH, the torsional angles indicate that neither the C$_{10}$ skeletons nor the substituents attached to them deviate strongly from coplanarity (Table 2). The N···P connecting lines deviate only slightly from the C$_{10}$ planes (N(1/2)—P—C(1/21)—C(2/22), 179.9, −172.5°, P—N(1/2)—C(8/28)—C(7/27), 176.9, −170.7°, and N(1/2)—P—C(1/21)—C(9/29), −7.5, 7.9°, P—N(1/2)—C(8)—C(9), −2.2, 10.1°). One of the N—C$_{\text{Me}}$ bonds is perpendicular to the pertinent C$_{10}$ plane or not far from orthogonality in the anticlinal sector, whereas the other one is on the other side of the C$_{10}$ plane in the anticlinal sector about half way between orthogonal and ecliptic. This unsymmetrical conformation is a wide-spread feature; it can be rationalized [1, 16] as the consequence of the "size" of the lone pair which a symmetrical arrangement of the Me groups would force into a position ecliptic to the C(1)—C(9) and P—C(1) bonds. Rotation by *ca.* 25° around the N(1/2)—C(8/28) bond would relieve this strain, but provides additional evidence that the lone pair is not involved in a N→P bond. The direction of the rotation is dictated by the relative bulk of the substituents at the P atom: The second DAN group resides on the same side of the C$_{10}$ plane as C(12/32) and consequently, the H atom at the same side as the (quasi-)orthogonal Me group. Surprisingly, one P—C$_{\text{DAN}}$ bond resides in the antiperiplanar sector, whereas the other one is perpendicular. The lone pairs at P and at N, then, point into directions at opposite sides of the C$_{10}$ planes and thus minimize electrostatic repulsion.

With respect to the question of N···H—P hydrogen bonds the distances d(P—H), d(N···H) and the angles N···H—P are of interest. d(P—H) = 133.7 pm and the two sets d(N(1)···P) = 279.1/d(N(1)···H) = 410.7 pm / angle N(1)···H—P 8.4° and d(N(2)···P) = 270.2 pm/d(N(2)···H) = 269.9 pm / angle N(2)···H—P 75.8° are unambiguous evidence that no N···H—P hydrogen bond exists [65]. This is not surprising, because phosphorus is more electropositive than carbon [31].

In conclusion, the structural data reveal intersubstituent repulsion which is relieved mainly by in-plane distortion of the naphthalene skeletons. They do not provide evidence for dative N→P interaction.

Table 2. Selected distances (pm), angles (°) and torsion angles (°) for (DAN)$_2$PH.

P-C21	185.0(2)	P-C1	185.4(2)
C8-N1	143.2(2)	N1-C11	146.3(2)
N1-C12	146.1(2)	N2-C28	142.7(2)
N2-C32	145.6(2)	N2-C31	146.2(2)
P-N1	279.1(2)	P-N2	270.2(1)
P-H1P	133.7(17)	N1-H1P	410.7(17)
N2-H1P	269.9(17)	C21-P-C1	102.5(1)
C2-C1-P	117.4(2)	C(9)-C(1)-P	124.3(1)
C(7)-C(8)-N(1)	121.0(2)	C9-C8-N1	118.3(2)
C8-C9-C1	124.0(2)	C4-C10-C5	120.1(2)
C(22)-C(21)-P	119.7(1)	C29-C21-P	122.3(1)
C(27)-C(28)-N(2)	122.2(2)	N(2)-C(28)-C(29)	117.4(2)
C28-C29-C21	123.7(2)	C(25)-C(30)-C(24)	120.3(2)
C1-P-H1P	93.0(7)	C21-P-H1P	95.4(7)
P-H1P-N1	8.4(5)	P-H1P-N2	75.8(7)
C21-P-C1-C2	97.1(2)	C1-P-C21-C22	19.5(2)
C21-P-C1-C9	−90.3(2)	C1-P-C21-C29	−160.0(2)
P-C1-C2-C3	173.2(2)	P-C21-C22-C23	−178.6(2)
C6-C7-C8-N1	−177.6(2)	C26-C27-C28-N2	−177.8(2)
N1-C8-C9-C10	178.6(2)	N2-C28-C29-C30	174.5(2)
N1-C8-C9-C1	−3.1(2)	N2-C28-C29-C21	−6.6(2)
P-C1-C9-C8	9.9(2)	P-C21-C29-C30	173.8(1)
P-C1-C9-C10	−171.9(1)	P-C21-C29-C28	−5.2(2)
C7-C8-N1-C12	−47.1(2)	C27-C28-N2-C32	−41.0(2)
C9-C8-N1-C12	133.8(2)	C29-C28-N2-C32	139.8(2)
C7-C8-N1-C11	79.8(2)	C27-C28-N2-C31	89.3(2)
C9-C8-N1-C11	−99.3(2)	C29-C28-N2-C31	−89.9(2)

NMR spectra of (DAN)$_2$PH

Depending on whether there are dative N→P interactions or not, (DAN)$_2$PH is either a sterically hindered secondary phosphine or a P-deprotonated di(hydrogeno)phosphate of the C$_2$(N$^+$)$_2$(P$^-$)H$_2$ type. Unfortunately, no authentic di(hydrogeno) phosphates R$_4$P$^-$H$_2$ nor their conjugate bases are available for comparison. On the other hand, primary and secondary phosphines exhibit much smaller $^1J(^{31}$P, ^{1}H) coupling constants than non-quaternary phosphonium salts [39] so that the ranges of phosphines and phosphoranes/phosphates are well separated. $^1J(^{31}$P, ^{1}H) thus gains increased significance.

The ^{31}P NMR spectrum of (DAN)$_2$PH exhibits a doublet at δ = − 22.85 ($^1J(^{31}$P, ^{1}H) = 208 Hz; Carre *et al.* [22]: −22.8 / 208 Hz), *i. e.* downfield by 17.85 ppm with respect to Ph$_2$PH [66] and hence at remarkably *lower* field than Ph(DAN)$_2$P with respect to Ph$_3$P ($\Delta\delta$ = *ca.* + 8.9 ppm [4, 12]) and not indicative of P-hypercoordination. On the other hand, δ((DAN)$_2$PH) is upfield by 27.25 ppm with respect to Ph(DAN)$_2$P [4]. Though smaller, the highfield shift parallels the same phenomenon in the series Ph$_n$PH$_{3−n}$, $\Delta\delta$ = *ca.* − 35 (n = 3/2), −81 (n = 2/1), −119 (n = 1/0) [67]. It is not known to what extent the various parameters which determine the signal position in the series

$Ph_{3-n}(DAN)_nP$ [12], are operative in corresponding secondary phosphines [68] so that no further rationalization is possible. It suffices to point out that *a)* a DAN-phosphorus compound with hexa-coordinate phosphorus in which a N→P bond did form, absorbed at much higher field though, in addition to the N atom of the DAN group, four O atoms were bound to the P atom ($\delta = -61.3$ [14]), and *b)* the phosphorane $(DAN)P(C_{12}H_8)_2$, in which N→P interaction has been concluded to play no role, exhibited $\delta = --85$ [68b].

The $^1J(^{31}P, ^1H)$ coupling constant of $(DAN)_2$PH is within the fairly narrow range of primary and secondary phosphines [39] (*ca.* 180–240 Hz [66, 69–72]), far distant from any $^1J(^{31}P, ^1H)$ value of hydrogeno-phosphoranes and -phosphates. $^1J(^{31}P, ^1H)$ is unaffected by steric congestion (2,4,6-$(tBu)_3C_6H_2PH_2$: 210.6 Hz [58]). $^1J(^{31}P, ^1H) = 208$ Hz thus is unambiguous evidence that in $(DAN)_2$PH the Me_2N groups do not engage in N→P bonds.

This result has an important consequence. The rigidity of the DAN-P structure precludes that the situation in solution differs from that in the crystal [73]. $^1J(^{31}P, ^1H)$ and the crystal structure of $(DAN)_2$PH thus provide the proof that an interatomic distance $d(N\cdots P) = 270$ pm occurs in a DAN-P compound in which there is no N→P interaction. This invalidates the key argument on which the claim of P-hypercoordination in DAN-P compounds is based, namely that N$\cdots$P distances of this length and longer, if shorter than $\Sigma r(vdW_{N,P})$, prove N→P dative bonding [6, 7].

The same coupling constant, $^1J(^{31}P, ^1H) = 208.0$ Hz, was found in the 200 MHz ^1H NMR spectrum (δ(P-H) = 5.84 (CDCl$_3$; Carre *et al.* [22]: $\delta = 6.0$, $J = 206$ Hz, CD$_2$Cl$_2$). At higher field, a sharp singlet, $\delta = 2.63$, and a broad signal, $\delta = 2.35$, were recorded for N(CH_3)$_2$ (at *ca.* +23 ℃) [74]; there was no ^{31}P—CH_3 coupling which in case of N→P bonding might have been expected ($^3J(^{31}P, ^1H)$ *via* C and N). The Me_2N signal pattern closely resembles that of (HO)(DAN)$_2$CH at +23 ℃ [10] so that again the same rationalization is likely to apply (*vide supra*). A stronger magnetic field would increase $\Delta\delta$ (in Hz) and thereby raise the temperatures required for the equilibration processes due to rotation around the P—C(1) bonds. In fact, at 500 MHz / +23 ℃ $(DAN)_2$PH gave a spectrum in which none of the Me signals was a sharp singlet. A very unsymmetrical, broad absorption indicated the superposition of broad signals. The 200 and 250 MHz ^1H NMR spectra of Ph(DAN)$_2$P, exhibiting *four* broadened signals at *ca.* 23 ℃, may in-dicate that under comparable conditions the process of equilibration is less advanced, *i. e.* that here the barrier of rotation around the P—C(1) bond is higher than in $(DAN)_2$PH. This is in line with more severe crowding in the tertiary phosphine than in the secondary phosphine whereas within the concept of N→P bonding it would be hard to be reconciled with the idea that donor→acceptor interaction would be facilitated in the secondary phosphine. However, no definite conclusion is possible, because the coalescence temperature depends on the separation of the respective signals which remained unknown for $(DAN)_2$PH. Low temperature 500 MHz spectra of $(DAN)_2$PH did not reveal the required four N(CH_3)$_2$ signals which may be the accidental consequence of small $\Delta\delta$ and hence very low coalescence temperatures.

Protonation studies on (DAN)$_2$PH

As before, protonation was achieved by the addition of various amounts of acid to $(DAN)_2$PH dissolved in CDCl$_3$ and monitored by ^{31}P and ^1H NMR. We did not encounter the instability which has been reported for **5e** both in solution and in air [22]. 1 equiv. of TsOH caused a protonation shift of +7.0 ppm, 1.8 times the effect in Ph(DAN)$_2$P. Further 0.5 equiv. of TsOH had a negligible effect upon $\delta(^{31}P)$; the proton-coupled spectrum exhibited a triplet indicating complete P-protonation and the presence of a P$^+$H$_2$ group. $^1J(^{31}P, ^1H) = 589.2/589.7$ Hz compares well with the coupling constant reported for **5e**, 590 Hz, whereas the signal position does not ($\delta = -16.0$ *vs.* -6.3 [22]). On the other hand, $\delta(^{31}P)$ is in good accord with that of **5f** ($\delta = -16.25$, in CD$_2$Cl$_2$) for which, however, a ^1J coupling constant smaller by 26 Hz had been reported [22]. The good agreement of $\delta(^{31}P)$ of the tosylate and the tetraarylborate complies with our previous experience that $\delta(^{31}P)$ is not subject to a measurable anion effect.

In the presence of 2 equiv. of TsOH, $^1J(^{31}P, ^1H) = 584/586$ Hz was recorded; the signals experienced an upfield shift to $\delta = -17.0$. 8.8 equiv. of TFA caused a signal position of -19.6 and $^1J(^{31}P, ^1H) = 561$ Hz, the latter in good agreement with the value of 564 Hz reported for **5f** [22]. The small additional highfield shift of $\Delta\delta = -2.6$ ppm seems more likely to be a solvent effect than an indication of N-protonation. While still exceeding the $^1J(^{31}P, ^1H)$ values of the reference material, $^1J(^{31}P, ^1H)$ is considerably smaller than the value for **5b** so that no N→P interaction needs to be invoked.

In the ^{31}P NMR spectra of (DAN)$_2$PH + TsOH the "outer" signals are well resolved triplets with $^3J(^{31}$P, 2-^{1}H) = 20.0 Hz, whereas the central one is a somewhat broadened signal without fine structure. 8.8 equiv. of TFA resolve also the latter so that a ^1J-triplet of three well resolved ^3J-triplets is recorded; $^3J(^{31}$P, 2-^{1}H) = 19.7 Hz, three times larger than $^3J(^{31}$P, ^{1}H) = 6.6 Hz in PhPH$_2$ [69]. Though slightly larger than $^3J(^{31}$P, ^{1}H) in **5b,d**, this value is still unconspicuous. The direction of the protonation shift is as expected for the creation of a positive charge at the P atom whereas a change of bonding in consequence of the improved conditions for N→P$^+$ interaction ought to have produced a *high*field shift. Again, then, no hypercoordination is indicated.

Conclusion

In summary, for the DAN-P$^+$—H salts an overall picture emerges from the δ and $^1J(^{31}$P, ^{1}H) data which is somewhat blurred by other factors but which indicates that N→P$^+$ bonding does not play a role. $^1J(^{31}$P, ^{1}H) of (DAN)$_2$PH proved decisive to discredit the basic assumption in the preceding discussion about N→P bonding in DAN-P compounds, namely that N···P distances in the range between *ca.* 270 pm and Σr(vdW$_{N,P}$) are proof of such interaction. Our results thus permit to arrive at a more realistic evaluation of the capability of phosphorus to attain hypercoordination. It seems likely that in the (DAN)hydrogenosilanes the situation is not much different.

Experimental Section

Synthesis

The elemental analysis was performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

Bis(8-dimethylamino-naphth-1-yl)phosphine. From 8.70 g (50.8 mmol) of 1-dimethylamino-naphthalene, dissolved in 10 ml of anhydrous diethylether, and 30.0 ml (48.0 mmol) of a commercial 1.6 M solution of *n*-butyl lithium in *n*-hexane, a suspension of crystalline 8-dimethylamino-naphth-1-yl lithium was prepared, as previously described [15]. At −78 °C 1.95 ml (22.3 mmol) of freshly distilled phosphorus trichloride was added within 45 min under vigorous stirring which was continued for 5 h. The mixture was then permitted to warm up to −2 °C within 15 h and stirred for another 2¾ h at r. t. Then a solution of *iso*-propyl-magnesium bromide prepared from 1.42 g (58.4 mg-atom) of magnesium turnings and 5.50 ml (58.8 mmol) of 2-bromo-propane in 30 ml of anhydrous diethylether was added within 5 min

under external cooling. The mixture was kept at room temperature for 70 h, then, after addition of 5 ml of anhydrous ethanol, followed by 30 ml of water and finally 3 ml of acetic acid, extracted with toluene/dichloromethane. After filtration through sodium sulfate/ silica gel the extract was evaporated and the yellow, liquid residue dissolved in 40 ml of boiling acetone. On standing at *ca.* −15 °C, 4.73 g of yellow crystals deposited. These consisted mainly of (DAN)$_2$PH and of some (DAN)$_3$P. Separation was performed according to Pasteur's method [75]; yield of (DAN)$_2$PH 4.45 g (53%), melting from 140 to 150 °C. – Analysis for C$_{24}$H$_{25}$N$_2$P (372.5): calcd. N 7.52, P 8.32; found N 7.80, P 8.22.

The tertiary phosphines are known compounds which were prepared by standard procedures.

Crystal structure determination of bis(8-dimethylamino-naphth-1-yl)phosphine

C$_{24}$H$_{25}$N$_2$P, MG = 372.46 g/mol, yellow block, monoclinic, space group $P2_1/n$ (no. 14), a = 11.472 (2), b = 10.674 (2), c = 17.167 (3) Å, β = 106.87 (1) °, V = 2011.7 (6) Å^3, T = 170 K, ρ_{calc} = 1.230 g·cm^{-3}, μ = 0.15 mm^{-1}, Z = 4, Nonius CAD4 four circle diffractometer, Mo-K_α (λ = 0.71073 Å), 9099 measured reflections in the range of 3° ≤ 2θ ≤ 56°, 4845 independent reflections used for refinement and 3801 reflections with $I \geq 2\sigma(I)$. Structure solution was performed using SHELXS-86. Structure refinement against F^2 using SHELXL-93. 252 refined parameters, R_1 for 3801 reflections with $I \geq 2\sigma(I)$ = 0.0394, wR_2 for all 4845 independent reflections = 0.1088, GoF 1.029, residual electron density: 0.37 / − 0.23 Å^{-3}. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C—H hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using the riding model. The hydrogen atom attached to the phosphorus atom was located from the difference map and refined with varying coordinates and isotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 195939. 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].

[1] 8th Communication: G. P. Schiemenz, Z. Anorg. Allg. Chem. **628**, 2597 (2002).

[2] *Cf.* A. Karaçar, V. Klaukien, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, R. Schmutzler, Z. Anorg. Allg. Chem. **627**, 2589 (2001).

[3] *E. g.*, $d(\text{P}\cdots\text{N}) = 262$ pm in DAN-P(C≡C—Ph)$_2$ where steric congestion in the *peri*-space is particularly small: C. Chuit, C. Reyé, Eur. J. Inorg. Chem. 1847 (1998).

[4] *E. g.*, $d(\text{P}\cdots\text{N}) = 301$ pm in Ph(DAN)$_2$PS where there is high steric congestion in the N/P region: M. Chauhan, C. Chuit, R. J. P. Corriu, C. Reyé, J.-P. Declercq, A. Dubourg, J. Organomet. Chem. **510**, 173 (1996).

[5] S. S. Batsanov, Izvest. Akad. Nauk, Ser. Khim. 24 (1995); Russ. Chem. Bull. **44**, 18 (1995).

[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. **32**, 1430 (1993).

[7] F. H. Carré, C. Chuit, R. J. P. Corriu, W. E. Douglas, D. M. H. Guy, C. Reyé, Eur. J. Inorg. Chem. 647 (2000).

[8] E. Fluck, G. Heckmann, in J. G. Verkade, L. D. Quin (eds): Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis (Methods in Stereochemical Analysis, **8**), 61 – 113, VCH Publishers, Deerfield Beach (1987).

[9] G. P. Schiemenz, E. Papageorgiou, Phosphorus Sulfur **13**, 41 (1982).

[10] G. P. Schiemenz, B. Schiemenz, S. Petersen, C. Wolff, Chirality **10**, 180 (1998).

[11] G. P. Schiemenz, Chem. Listy **92**, 269 (1998).

[12] G. P. Schiemenz, Phosphorus, Sulfur, Silicon Relat. Elem. **163**, 185 (2000).

[13] G. P. Schiemenz, R. Bukowski, L. Eckholtz, B. Varnskühler, Z. Naturforsch. **55b**, 12 (2000).

[14] G. P. Schiemenz, S. Pörksen, C. Näther, Z. Naturforsch. **55b**, 841 (2000).

[15] G. Dyker, M. Hagel, G. Henkel, M. Köckerling, C. Näther, S. Petersen, G. P. Schiemenz, Z. Naturforsch. **56b**, 1109 (2001).

[16] G. P. Schiemenz, S. Pörksen, P. M. Dominiak, K. Wozniak, Z. Naturforsch. **57b**, 8 (2002).

[17] G. P. Schiemenz, C. Näther, Z. Naturforsch. **57b**, 309 (2002).

[18] C. A. Streuli, Anal. Chem. **31**, 1652 (1959).

[19] C. A. Streuli, Anal. Chem. **32**, 985 (1960).

[20] G. P. Schiemenz, Tetrahedron **27**, 3231 (1971).

[21] Y. Yamashoji, T. Matsushita, M. Tanaka, T. Shono, M. Wada, Polyhedron **8**, 1053 (1989). The additivity of the effect of up to six *ortho*-methoxy groups rules out σ-donation O→P as the cause of this dramatic increase of basicity.

[22] F. Carre, M. Chauhan, C. Chuit, R. J. P. Corriu, C. Reye, Phosphorus, Sulfur, Silicon Relat. Elem. **123**, 181 (1997).

[23] A. Chandrasekaran, N. V. Timosheva, R. O. Day, R. R. Holmes, Inorg. Chem. **39**, 1338 (2000).

[24] *Cf.* Schiemenz [12], note 21; Schiemenz *et al.* [13], note 6.

[25] S. O.Grim, A. W. Yankowsky, Phosphorus Sulfur **3**, 191 (1977).

[26] S. O. Grim, A. W. Yankowsky, J. Org. Chem. **42**, 1236 (1977).

[27] S. O. Grim, W. McFarlane, E. F. Davidoff, T. J. Marks, J. Phys. Chem. **70**, 581 (1966) (in DMSO).

[28] Note that the melting points of our sample and that of Corriu *et al.* differ by 14°. To our experience, polymorphism is frequent in phosphonium salts and other organophosphorus compounds.

[29] Replacement of Ph by Me in (DAN)(PhCH$_2$)Ph$_2$P$^+$ Br$^-$ is thus more effective than introduction of 8-Me$_2$N into (α-C$_{10}$H$_7$)(PhCH$_2$)Ph$_2$P$^+$ Br$^-$ [7].

[30] G. P. Schiemenz, Phosphorus **3**, 125 (1973).

[31] L. Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals, 2nd ed., p. 60, 64, Cornell U. P., Ithaca NY (1945), 3rd ed., p. 90, *ibid.* (1960).

[32] R. W. Alder, P. S. Bowman, W. R. S. Steele, D. R. Winterman, J. Chem. Soc., Chem. Commun. 723 (1968); H. A. Staab, T. Saupe, Angew. Chem. **100**, 895 (1988), Angew. Chem. Int. Ed. **27**, 865 (1988).

[33] R. W. Alder, M. R. Bryce, N. C. Goode, J. Chem. Soc., Perkin Trans. 2, 477 (1982).

[34] C. Brelière, R. J. P. Corriu, G. Royo, J. Zwecker, Organometallics **8**, 1834 (1989).

[35] The NMR data reported for Ph(DAN)$_2$P$^+$H [43] are not in full agreement with our results. We refrain from a comment.

[36] *Cf.* Schiemenz *et al.* [14], Table 1.

[37] J. G. Verkade, J. A. Mosbo, in: Verkade, Quin [8] 425 – 463, p. 428.

[38] *Cf.* Carré *et al.* [7], formulae **9** and **10**.

[39] J. F. Brazier, D. Houalla, M. Loenig (Koenig), R. Wolf, Topics in Phosphorus Chemistry **8**, 99 – 192 (1976), pp. 104 – 109. A considerable increase of $^1J(^{31}\text{P}, ^1\text{H})$ in a N$_2$O$_2$PH phosphorane upon coordination of one of the heteroatoms attached to P

with BF_3 or of two heteroatoms with $ZnCl_2$ is in line with the enhancement of the effective electronegativity caused by the coordination (K. N. Gavrilov, A. V. Korostylev, P. V. Petrovskiy, A. Yu. Kovalevsky, V. A. Davankov, Phosphorus, Sulfur Silicon Relat. Elem. **155**, 15 (1999); *cf.* A. V. Korostylev, O. G. Bondarev, K. A. Lyssenko, A. Yu. Kovalevsky, P. V. Petrovskii, G. V. Tcherkaev, I. S. Mikhel, V. A. Davankov, K. N. Gavrilov, Inorg. Chim. Acta **295**, 164 (1999)).

[40] D. Hellwinkel, Chem. Ber. **102**, 528 (1969).

[41] M. R. Ross, J. C. Martin, J. Am. Chem. Soc. **103**, 1234 (1981). The phenomenon is paralleled by $^1J(^{31}P, ^{19}F)$ in MeF_3PH: $^1J(^{31}P, ^{19}F_{ap}) = 795$, $^1J(^{31}P, ^{19}F_{eq}) = 965$ Hz (A. Kornath, F. Neumann, R. Ludwig, Z. Anorg. Allg. Chem. **628**, 1835 (2002)). In P-hydrogeno-azaphosphatranes, where the H atom is apical by necessity, the three electronegative N atoms raise $^1J(^{31}P, ^1H)$ to $453 – 506$ Hz (M. A. H. Laramay, J. G. Verkade, J. Am. Chem. Soc. **112**, 9421 (1990)), hence only into the range of protonated tert. phosphines.

[42] L. Pauling [31], 2nd ed., pp. 65-66.

[43] F. Seel, W. Gombler, K. H. Rudolph, Z. Naturforsch. **23b**, 387 (1968); F. Seel, K. Rudolph, Z. Anorg. Allg. Chem. **363**, 233 (1968). Replacement of one Me group by an equatorial fluorine atom increases $^1J(^{31}P, ^1H)$ by 114 Hz: Kornath *et al.* [41].

[44] J. F. Nixon, J. R. Swain, J. Chem. Soc., Chem. Commun. 997 (1968).

[45] M. Wieber, K. Foroughi, Angew. Chem. **85**, 444 (1973); Angew. Chem. Int. Ed. **12**, 419 (1973).

[46] M. Wieber, K. Foroughi, H. Klingl, Chem. Ber. **107**, 639 (1974).

[47] W. McFarlane, R. F. M. White, J. Chem. Soc., Chem. Commun. 744 (1969).

[48] S. Berger, S. Braun, H.-O. Kalinowski, NMR Spectroscopy of the Non-Metallic Elements, pp. 911-918, John Wiley & Sons, Chichester, New York, Weinheim, Brisbane, Singapore, Toronto (1997).

[49] Berger, Braun, Kalinowski [48], pp. 917, 919.

[50] *Cf.* F. B. Mallory, C. W. Mallory, M.-C. Fedarko, J. Am. Chem. Soc. **96**, 3536 (1974); R. D. Jackson, S. James, A. G. Orpen, P. G. Pringle, J. Organomet. Chem. **458**, C3 (1993); A. Karaçar, M. Freytag, P. G. Jones, R. Bartsch, R. Schmutzler, Z. Anorg. Allg. Chem. **628**, 533 (2002).

[51] F. B. Mallory, J. Am. Chem. Soc. **95**, 7747 (1973).

[52] Surprisingly, also the quaternary salt $Me_2(PhCH_2)(DAN)P^+ Br^-$ has been reported to be *very air sensitive* [7]. We did not observe such property of the closely related salts $Ph_2(PhCH_2)(DAN)P^+ Br^-$ [9] and $Me_2(Ph)(DAN)P^+ I^-$ [16].

[53] Carre *et al.* [22], p. 194.

[54] Carre *et al.* [22], p. 188.

[55] G. P. Schiemenz, Angew. Chem. **83**, 929 (1971); Angew. Chem. Int. Ed. **10**, 855 (1971); J. Magn. Reson. **6**, 291 (1972); J. Organomet. Chem. **52**, 349 (1973); Org. Magn. Reson. **5**, 257 (1973); J. Mol. Structure **16**, 99 (1973), Tetrahedron **29**, 741 (1973); G. P. Schiemenz, H. Rast, Tetrahedron Lett. 1697 (1972); G. P. Schiemenz, H.-P. Hansen, Angew. Chem. **85**, 404 (1973); Angew. Chem. Int. Ed. **12**, 400 (1973); G. P. Schiemenz, P. Klemm, Org. Magn. Reson. **6**, 276 (1974); G. P. Schiemenz, R. Hinz, Phosphorus Sulfur **18**, 237 (1983).

[56] G. Boche, Angew. Chem. **104**, 742 (1992); Angew. Chem. Int. Ed. **31**, 731 (1992). Interpenetration of non-spherical counter ions is implied by the rationalization [55] that, due to Coulomb attraction, the centers of charge approach each other as closely as possible. Enantiotopic protons in the vicinity of the center of positive charge in achiral cations become diastereotopic by ion pair association with bulky chiral anions (G. P. Schiemenz, J. Pistor, in L. D. Quin, J. Verkade (eds): Phosphorus Chemistry [ACS Symposium Series **171**], pp. 567 – 570 (1981); G. P. Schiemenz, J. Pistor, M. Wolf, Chem. Scripta **18**, 67 (1981); G. P. Schiemenz, J. Pistor, Chem. Scripta **23**, 216 (1984)). This phenomenon presupposes interpenetration of the counter ions.

[57] G. P. Schiemenz, unpublished. – This is in accord with our rationalization of the tetraphenylborate effect [55]: The centres of charge, P^+ and B^-, approach each other as closely as possible. Protons in α-position to P^+ thus reside above one of the Ph rings and are shielded by the extra field of the ring current. This extra field causes a highfield shift of ca. 1 ppm which is much in ^1H NMR but almost negligible in ^{31}P NMR. Second, P^+ does not reside above one of the Ph rings, but rather in the "dead angle".

[58] A similar resistance against autoxidation has been observed for 2,4,6-tri(*tert*-butyl)phenylphosphine (M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, K. Nishimoto, J. Am. Chem. Soc. **105**, 2495 (1983)) and is presumably a consequence of the steric congestion around the P atom. Air-stable primary phosphines in which no steric protection of the PH_2 group is obvious, have recently been reported: W. Henderson, S. R. Alley, J. Organomet. Chem. **656**, 120 (2002).

[59] To our experience, melting ranges rather than sharp melting points as well as polymorphism are not infrequent among phosphines. *E. g.*, for 2,4,6-tri(*tert*-butyl)phenylphosphine melting points of 80 °C

(K. Issleib, H. Schmidt, C. Wirkner, Z. Anorg. Allg. Chem. **488**, 75(1982)), of 144 °C (A. H. Cowley, J. E. Kilduff, T. H. Newman, M. Pakulski, J. Am. Chem. Soc. **104**, 5820 (1982)) and of 150–152 °C [58] have been reported.

[60] Carre *et al*. [22], p. 191. Note that the formula and the values calculated for C and H require revision; m/e = 372 corresponds to M^+ rather than $(M—H)^+$ (unless it is meant to refer to $^{13}C_1—M$).

[61] J. J. Daly, J. Chem. Soc. 3799 (1964).

[62] C. Brelière, F. Carré, R. J. P. Corriu, M. Poirier, G. Royo, J. Zwecker, Organometallics **8**, 1831 (1989).

[63] R. O. Day, R. R. Holmes, Inorg. Chem. **19**, 3609 (1980).

[64] Compare the data of $(DAN)_2PH$ (Table 2) with those of $Ph(DAN)_2P^+H\ Br^-$ [22].

[65] G. R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, Oxford (1999/2001); G. R. Desiraju, Acc. Chem. Res. **35**, 565 (2002).

[66] G. A. Olah, C. W. McFarland, J. Org. Chem. **34**, 1832 (1969).

[67] V. Mark, C. H. Dungan, M. M. Crutchfield, J. R. van Wazer, Topics in Phosphorus Chemistry **5**, 227–457 (1967), pp. 239, 243, 246, 250.

[68] Note that in the series of bis(2,2'-biphenyl-ylene)phosphoranes R-$P(C_{12}H_8)_2$ $\delta(^{31}P)$ is the same for R = Ph, α-$C_{10}H_7$ and DAN, whereas replacement of Ph by H results in a highfield shift of $\Delta\delta$ = −27 ppm (*a*) Hellwinkel [40]; *b*) D. Hellwinkel, W. Lindner, H.-J. Wilfinger, Chem. Ber. **107**, 1428 (1974)).

[69] J. W. Akitt, R. H. Cragg, N. N. Greenwood, J. Chem. Soc., Chem. Commun. 134 (1966).

[70] M. G. Barlow, M. Green, R. N. Haszeldine, H. G. Higson, J. Chem. Soc. B 1025 (1966).

[71] D. J. Brauer, J. Fischer, S. Kucken, K. P. Langhans, O. Stelzer, Z. Naturforsch. **49b**, 1511 (1994); N. J. Goodwin, W. Henderson, B. K. Nicholson, J. Chem. Soc., Chem. Commun. 31 (1997); N. J. Goodwin, W. Henderson, B. K. Nicholson, J. Fawcett, D. R. Russell, J. Chem. Soc., Dalton Trans. 1785 (1999); W. Henderson *et al*. [58].

[72] M. Brynda, M. Geoffroy, G. Bernardinelli, J. Chem. Soc., Chem. Commun. 961 (1999).

[73] G. van Koten, Pure Appl. Chem. **62**, 1155 (1990).

[74] Carre *et al*. [22] reported only one singlet at δ = 2.6 for all 12 Me protons (250 MHz, CD_2Cl_2), presumably at *ca*. 25 °C.

[75] See, for example: N. L. Allinger, M. P. Cava, D. C. de Jongh, C. R. Johnson, N. A. Lebel, C. L. Stevens, Organische Chemie, p. 208, Walter de Gruyter, Berlin, New York (1980).