peri-Interactions in Naphthalenes, 11 [1]. A New Approach to the Investigation of Dative *peri* Bonding

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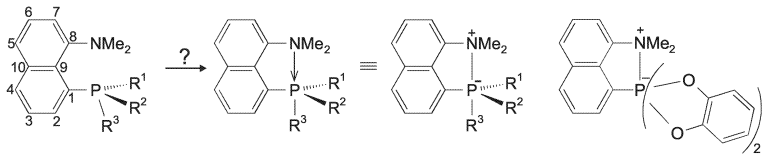
The failure of the *sum of van der Waals radii axiom* to provide information about donor-acceptor interactions in 8-dimethylamino-naphth-1-yl phosphines and their derivatives called for alternative methods. The coupling constants J(C,H) of the Me_2N groups proved useful and indicate that in these compounds, N→P interactions are negligible.

Key words: Octet Rule, Naphthalene *peri*-Interactions, N→P Bonding, ^1J and ^3J(C,H) Coupling

Introduction

peri-Disubstituted naphthalenes (*pDSN's*, **1**, R^3 = or $\neq$ H; see Table 1) are a good testing ground for the scope of three rules [2] which proved useful to channel the multitude of details of organic chemistry [3]. The first two rules are a phenomenological version of G. N. Lewis' *octet rule* [4] and a generalization of the formation of covalent bonds by reaction between *Lewis acids* and *bases* (*electrophiles* and *nucleophiles* in C. K. Ingold's terminology). The third rule concerns the support which intramolecular reactions receive if five- or six-membered rings are to be formed. Rule 1 insists on the tetracovalency of carbon (mono-, di-, tricovalency of hydrogen, oxygen and nitrogen, respectively, all uncharged), but is subject to exceptions for the respective third period elements (and "higher" elements) which, under favourable conditions, exhibit electrophilic properties and are thus capable of becoming *hypercoordinate* by reaction according to rule 2, a process aided by ring formation according to rule 3. As a prerequisite for bonding interaction, the electrophilicity and nucleophilicity of the reaction partners must surpass a certain minimum. Recent interest has been focussed on *Lewis acid* (electrophilic) properties of phosphorus in phosphines in which no electronegative atoms are bound to the P center [5]. In intermolecular interactions, the phosphorus of tertiary phosphines and most of their derivatives is devoid of electrophilic properties even towards strong nucleophiles such as organo-lithium or Grignard reagents. In (8-dimethylamino-naphth-1-yl) ("*DAN*") phosphines (DAN-PR^1R^2; Scheme 1, formula **2a**) and their derivatives, the P atom conceivably could act as an electrophile towards the nucleophilic N atom residing in its vicinity (Scheme 1, formulae **3A**/**B**). The poor reactivity of dimethyl-(naphth-1-yl)-amine (**1**, $R^1 = Me_2N$, $R^2 = R^3 = H$) towards methyl iodide [6] attests only a mediocre nucleophilicity to the Me_2N group; however, the phenomenon may be caused by the steric congestion in the *peri* space and therefore have no bearing on an *intra*molecular donor-acceptor interaction. Forma-



2 3A 3B 1i

2, 3A, B	R^3
a	lone pair
b	H
c	alkyl

P = P^+ in **2b**, **c**, uncharged in **3Bb**, **c**

Scheme 1. Potential N→P interactions in DAN-phosphines **2a** and their derivatives in compliance with rules 2 and 3, violating rule 1.

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Table 1. NMR data of the substituted naphthalenes **1a** – **v** and related compounds.

				^{1}H NMR N-CH_3[1]		^{13}C NMR N-CH_3[1]		N-*C*-*H*	*C*-N-C-*H*	R^1-*C*^{2}
1	R^1	R^2	R^3	δ [ppm]	$\Delta\delta$ [ppm]	δ [ppm]	$\Delta\delta$ [ppm]	^1J [Hz]	^3J [Hz]	δ [ppm]
1a [19]	Me_2N	H	Ph_2P	2.90[3] [19]		44.93		134.9	4.6	152.37
1b [19]	Me_2N	H	$Ph_2(O)P$	2.93[3] [19]		44.63		135.5	4.3	155.44[4]
1c[5] [19]	Me_2N	H	$Ph_2(S)P$	2.94		44.66		135.7	4.4	155.37[6]
1d [35]	Me_2N	DAN	H	1.58[7]		41.00		133.6	4.8	151.72
				1.63[7]		47.63		134.5	4.4	151.64
1e	Me_2N	(HO)(Ph)(H)C	H	2.38		46.21		135.6	4.8	150.43
				2.72		47.69		135.7	4.9	
1f [36]	Me_2N	Me_2N	H	2.71[8]		44.30[8]		134.5	4.4	150.92
1g[9] [6]	Me_3N^{+}[10]	H	H	3.92[11]	(1.01[12])	57.07		145.0	n.r.	(141.22)
1h	Me_2N^{+}—	C(H)Ph	H	2.96		52.61		146.2	n.r.	(146.75)
				3.87		55.15		146.2	n.r.	
1i [8]	Me_2N^{+}—	$P^{-}(O_2C_6H_4)_2$	H	2.78 [8]		49.77		(145.5[13])	n.r.	(145.83)
				3.46 [8]		52.01				
1j[14]	$Me_2(H)N^{+}$	H	Ph_2P	3.46	**1a**/**j**: 0.56	47.14	**1a**/**j**: 2.21	144.9	3.9	(141.21)
1a+**1j**[15]	Me_2N + $Me_2(H)N^{+}$	H	Ph_2P	3.34	0.44	46.54	1.61	142.7	3.9	(142.63)
1k[16]	$Me_2(H)N^{+}$	H	$Ph_2(O)P$	3.42	**1b**/**k**: 0.49	46.96	**1b**/**k**: 2.34	145.3	3.7	(142.78)
1l[17]	$Me_2(H)N^{+}$	H	$Ph_2(S)P$	3.41	**1c**/**l**: 0.47	47.31	**1c**/**l**: 2.64	145.7	3.8	(141.78)
1m[18]	$Me_2(H)N^{+}$	DAN-H^{+}	H	*ca.* 2.75[19]	**1d**/**m**: 1.1-1.2	47.59	**1d**/**m**:6.59 -0.04	145.3	n.r.	(141.01)
1n[20]	$Me_2(H)N^{+}$	Me_2N	H	3.10[21]	**1f**/**n**:0.39	46.26[21]	**1f**/**n**:1.97	140.7	4.2	(144.39[22])
1o [19]	Me_2N	Ph_2P	H	2.27 [19]		46.11[23]		135.1	4.7	152.18[24]
1p[25]	Me_2N	$Ph_2(H)P^{+}$	H	2.32	**1o**/**p**: (0.05[26,27])	45.75	**1o**/**p**: (-0.36[28])	137.1	4.4	148.60
1q [16]	Me_2N	$Ph_2(O)P$	H	(2.10[29])		46.22		136.1	4.6	152.29[30]
1r [10]	Me_2N	(DAN)(Ph)(S)P	H	(1.05[31,32])		43.88		134.0	4.5	154.18[33]
				(1.13[31,34])		45.11		135.4	(4.8)[35]	154.26[33]
				(1.15[31,32])		46.35		135.0	n.r.	
				(1.18[31,34])		46.49		134.8	4.8	
				(2.00[31,32])		48.77		135.0	(5.3)[35]	
				(2.45[31,34])		48.96		134.4	4.7	
				(2.75[31,32])		49.18		136.1	5.1	
				(2.85[31,34])		49.41		134.5	(5.3)[35]	
1s [13]	Me_2N	$(DAN)_2P$	H	1.47[36]		45.74		134.3	4.6	154.12[37]
				2.70[35]		48.66[38]		134.0	4.8	
1t[39]	Me_2N	$(DAN)_2(H)P^{+}$	H	1.43[40]	**1s**/**t**: (-0.04[28])	46.62	**1s**/**t**: (0.88[26])	136.2	4.8	150.51
				2.75	**1s**/**t**: (0.05[26])	48.51	**1s**/**t**: (-0.15[28])	135.3	4.7	
1u[41]	$Me_2(H)N^{+}$	$Ph_2(O)P$	H	3.17	**1q**/**u**: 1.07	47.76	**1q**/**u**: 1.54	144.5	3.3	(142.91)
1v[42]	$Me_2(H)N^{+}$	(DANH^{+})(Ph)(S)P	H	1.00[34]	-[43]	-[44]		(144.6[44])	n.r.	(141.22)
				1.10[32]						
				1.58[34]						
				2.20[32]						
				2.43[32]						
				3.29[34]						
				3.38[32]						
				3.62[34]						

tion of a *dative* bond (N→P) according to rule 2 (hence violation of rule 1) would lead to a five-membered ring (as in **1i**, Scheme 1) in formal compliance with rule 3. However, the domain of the phenomena covered by rule 3 is aliphatic chemistry where five- and six-membered rings are almost unstrained and compatible with natural bond angles. In *p*DSN's, the validity of rule 3 (as well as that of rule 2) is curtailed by the rigidity of the naphthalene skeleton. Since the new bonds to be formed are much shorter than the distance d(C(1)···C(8)) in undeformed *p*DSN's, ring closure in the latter is opposed by a severe distortion of the naph-

Table 1 (continued).

5–6	Formula	^{1}H NMR N-CH_3[1] δ [ppm]	$\Delta\delta$ [ppm]	^{13}C NMR N-CH_3[1] δ [ppm]	$\Delta\delta$ [ppm]	N-*C*-*H* ^1J [Hz]	*C*-N-C-*H* ^3J [Hz]	R^1-*C*^{2} δ [ppm]
5a	$C_6H_5NMe_2$	2.97		40.47		135.1	4.1	150.92
5a + **5d**[45]	$C_6H_5NMe_2$ + $C_6H_5N^+(H)Me_2TsO^-$	3.03		42.58		138.2	4.0	148.13
5d[46]	$C_6H_5N^+(H)Me_2TsO^-$	3.16	**5a**/**d**: 0.19	46.76	**5a**/**d**: 6.29	144.7	3.7	(142.61)
5b	4-Me_2N-C_5H_4N	2.96		38.88		136.41	3.6	154.31
5c [37]	4-O_2N-$C_6H_4NMe_2$	3.09		40.15		137.1	3.6	154.40
6a [38]	(4-Me_2N-C_6H_4)$_3$COH	2.92		40.49		135.1	4.0	149.57
6b[47]	[(4-Me_2N-C_6H_4)$_3$C]$^+$ TsO^-	3.25		40.54		138.3	3.5	155.48

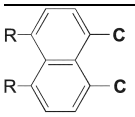
Notes: General: DAN = 8-dimethylamino-naphth-1-yl; DAN-H$^+$ = N-protonated DAN, $Me_2(H)N^+$-$C_{10}H_6$; $O_2C_6H_4$ = 1,2-phenylene-dioxy; n.r. = not resolved. Unless otherwise stated: singlets; solvent CD_2Cl_2; salts: anion 4-Me-C_6H_4-SO_3^- (TsO^-) (δ (H [Me]) = 2.27 – 2.31; δ(C [Me]) = 21.01 – 21.16 (average between TsO^- and excess TsOH except in **1h**, $\delta = 20.83$, and in **1n**, $\delta = 20.99$), qt, ^1J(C, H [Me]) = 126.6 – 126.9 Hz (**1h**: 126.3 Hz), ^3J(C[Me], 3,5-H) = 4.3 – 4.4 Hz) (cations and salts thereof have been assigned the same numbers); $\Delta\delta$ = N-protonation shift.

1. $\Delta\delta$ in parentheses in the cases of non-identical solvents. – 2. Data in parentheses refer to the signals at lowest field. Unlike the Me_2N-*C*(8) signals, they are not clearly separated from the other ^{13}C(sp^2) signals, and their assignment remains open. – 3. In $CDCl_3$. – 4. d, $\Delta\delta$ = 2.9 Hz; presumably ^4J(C, P). – 5. δ(P) = 41.62 (81.014 MHz). – 6. d, $\Delta\delta = 2.8$ Hz; presumably ^4J(C, P). – 7. m. p. 134 – 135 °C. Non-equivalent N-methyl groups because of hindered rotation. δ(H) (300 MHz, in $CDCl_3$): Highfield positions because of aromatic ring current shielding by the second C_{10} system (in C_6D_6: δ = 2.59, 2.63 [35]). δ(*C*H$_3$)(in $CDCl_3$) = 41.12, 47.69, *i. e.* virtually no solvent effect. – 8. In CCl_4 [36]; δ (C*H*$_3$) = 2.75, δ (^{13}C{^{1}H}) = 44.60, in CD_3CN [39]. – 9. In $(CD_3)_2SO$ because of insufficient solubility in CD_2Cl_2. – 10. Anion: I^-. – 11. $\delta = 4.03$ in CD_3OD [40], 4.12 in CF_3COOH [41]. – 12. Quaternization shift, **1g** *vs.* 1-$Me_2NC_{10}H_7$ (δ = 2.91 in $CDCl_3$ [19]). – 13. In $CDCl_3$ (δ (^{13}C{^{1}H}) = 49.68, 51.89); poorly resolved ^{1}H-coupled spectrum because of low solubility and superposition of ^2J(*C*-N-*P*) and ^3J(*C*-N-C-*H*) couplings. 145.5 Hz is the average value of four intersignal distances of 146.4, 145.0, 145.8, 144.9 Hz at $\delta = 49.75$, 49.96, 51.88 and 51.95 ppm, respectively. – 14. **1a** + 1.7 equivs of TsOH; possibly **1j** + some **1** (R^1 = $Me_2(H)N^+$, R^2 = H, R^3 = $Ph_2(H)P^+$) [23]. – 15. **1a** + 0.74 equivs of TsOH. – 16. **1b** + 1.6 equivs of TsOH. – 17. **1c** + 2.4 equivs of TsOH. – 18. **1d** + 2.0 equivs of TsOH per DAN group. – 19. One very broad signal because of incompletely hindered rotation. – 20. **1f** + 1.6 equivs of TsOH. ^2J(*C*-N-*H*) = 1.4 Hz. – 21. 200.13 MHz; ^3J(*H*$_3$C-N-*H*) = 2.4 Hz (Alder *et al.* [36]: δ (C*H*$_3$) = 3.21, $^3J = 2.0$ Hz, **1f** in CF_3COOH; Brycki *et al.* [39]: δ (C*H*$_3$) = 3.10 – 3.13, $^3J = 2.5$ Hz, δ (^{13}C{^{1}H}) = 46.71 – 46.84, various anions, in CD_3CN). – 22. Broadened signal in the ^{1}H-coupled spectrum. – 23. d, ^5J(C, P) = 7.6 Hz (tentative assignment). – 24. d, $\Delta\delta = 3.5$ Hz; presumably ^3J(C,P). – 25. **1o** +2.0 equivs of TsOH. – 26. Very small downfield shift caused by P-protonation. – 27. A broad signal at $\delta = 8.7$ presumably results from averaging between P$^+$-^1H and excess TsOH and thus indicates that P-protonation is still kinetically unstable; see **1t**. – 28. Minute *high*field shift caused by P-protonation. – 29. 250 MHz, $CDCl_3$ [16]. – 30. d, $\Delta\delta = 1.9$ Hz; presumably ^3J(C,P). – 31. 250 MHz, C_6D_6 [10]. – 32. Minor isomer. – 33. $\Delta\delta = 5.4$ Hz: Either ^3J(C,P), or δ(C(8)) of the two isomers, or δ(C(8)) of the two non-equivalent DAN groups within one isomer. – 34. Major isomer. – 35. Uncertain because of poor resolution. – 36. In $CDCl_3$: $\delta = 1.4$, 2.8 [13]; 1.46, 2.82 [17]. – 37. d, $\Delta\delta = 3.8$ Hz; presumably ^3J(C,P). – 38. d, $\Delta\delta = 11.6$ Hz; presumably *J*(C, P), through space coupling. – 39. **1s** + 2.8 equivs of TsOH per P atom. ^{13}C NMR at 50.323 MHz because of serious signal coincidences at 75.468 MHz. – 40. δ(P-*H*) = 10.37, d, ^1J(H,P) = 691.7 Hz. – 41. **1q** + 1.3 equivs of TsOH. – 42. **1r** + *ca.* 2.8 equivs of TsOH per DAN group. – 43. **1r**/**v**: No $\Delta\delta$ values can be given, because it is unknown whether the major isomer of **1v** corresponds with the major isomer of **1r**, *etc.* The same uncertainty applies to the stereochemical identity of the four N-Me groups within a molecule of each isomer. – 44. Poorly resolved ^{1}H-coupled spectrum because of signal broadening due to restricted rotations and signal overlap. 144.6 Hz is the average value of four intersignal distances of 145.4, 147.7, 142.0, 143.1 Hz at $\delta = 43.60$, 47.50, 48.39 and 49.39 ppm, respectively. No distances in the range 135 ± 2 Hz were observed. The data of **1u** should be considered with reserve. – 45. **5a** + 0.33 equivs of TsOH. – 46. **5a** + 1.3 equivs of TsOH. – 47. **6a** + 1.02 equivs of TsOH.

thalene skeleton (*e. g.* of the angles H_2C–C(1/8)–C(9) from 120° to 107.7/108.8° in acenaphthene (**4**, **C**/**C** = CH_2–CH_2, R = H) [7], P–C(1)–C(9) and N–C(8)–C(9) from 120° to 116.1 and 114.1°, respectively, in **1i** [8]) which would have to be energetically overruled by the bond energy of the new covalency. N, P-Substituted *p*DSN's such as DAN-phosphines would thus grant an insight into the scope of the rules and borderline cases of P-electrophilicity.

Previous attempts to gain such insight are based entirely on the presently much cherished axiom that all interatomic distances, including intramolecular ones, shorter than the sum of the respective van der Waals radii, Σr(vdW), are evidence of some sort of covalent bonding. For example, in the DAN-phosphine sulfide **1r** ((DAN)$_2$(Ph)PS), the distance d(N···P) is 301 pm, 7.4% shorter than $\Sigma r(\mathrm{vdW}_{N,P})$ = 325 pm [9]; it has been interpreted as evidence of an (albeit weak) bonding donor-acceptor interaction, hence an anisotropic attraction of covalent nature between the *peri*-substituents, N as the donor and P as an acceptor, for which the symbol of a *dative bond*, N→P, has been used [10 – 12]. In 1,8-di(carbon-substituted) naphthalenes, **4**, d(C···C) distances of 293 – 305 pm have

Table 2. C-Substituted pDSN's.



4

4	**C**	R	*d*(C–C) (pm)
a	Me	H	293.2 [32]
b	Ph	Ph	294.5 [33]
c	Ph	H	299.3 [33]
d	CH_2Br	H	305 [34]

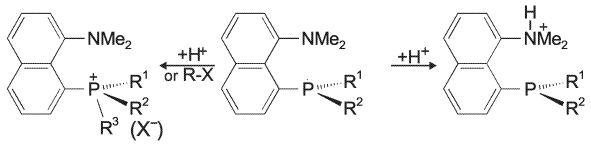
been found, shorter than $\Sigma r(\mathrm{vdW}_{C,C})$ = 340 pm [9] by 10 – 14% (*cf.* Table 2). If the Σr(vdW) axiom is accepted, these "forshortenings" are *proof of hypercoordinated carbon* [13]. However, since the geometry of the fairly rigid naphthalene skeleton deprives *peri*-substituents, whatever their nature, of any chance to attain the Σr(vdW) distance, it is more appealing to discard the Σr(vdW) axiom than to question the stringent validity of rule 1 [14]. Such clear-cut cases invalidate the Σr(vdW) axiom for *all p*DSN's, including those with potential N→P interaction. A valid appreciation depends therefore on the availability of criteria independent of Σr(vdW).

For the description of amine oxides, both the *Lewis formula* R_3N^+–$\underline{O}|^-$ and its coordination chemistry equivalent R_3N→O [15] are common. Similarly, for DAN-P compounds, the symbol N→P indicating *coordinate interactions* [10 – 12, 16 – 18] as well as the corresponding *Lewis formulae* have been used, N^+–P^- in phosphines DAN-PR_2 and λ^6-phosphates, N^+–P in phosphonium cations DAN-P^+R_3 [1, 8, 19 – 23] (see Scheme 1, formulae **1i**, **3A** and **3B**). The latter express more clearly a depletion of electron density at the N atom [24]. It has long been known that "*the dependence of* ^{13}C–^1H *coupling constants on the electronegativity* (hence, the effective electron density) *of attached groups offers an ideal way to detect the amount of positive charge*" [25]. The series of $^1J(^{13}C, {}^1H)$ values in H_3C-Hal (151.1, 151.5, 150.0, 149.1 Hz for I, Br, Cl, F, respectively [26]) fails to comply with this generalization and precludes a detailed interpretation of minute effects. However, the method seems reliable if restricted to a series of methyl compounds in which the nature of the atom bearing the Me group remains unchanged, as shown by the following examples: ^1J(C,H) of Me_3N, 131 Hz, Me_3N^+–$\underline{O}|^-$ and Me_3N^+–H 143 Hz, Me_3N^+–OH 144 Hz, Me_4N^+ 145 Hz; Me_2N–C(Me)=O⟷Me_2N^+=C(Me)–O^- with a partial charge on the N atom, 138 Hz [25]. ^1J(C, H) = 126.6 – 126.9 Hz of 4-H_3C-$C_6H_4SO_3^-$ (see Table 1) compares well with ^1J(C,H) = 125 Hz in CH_4 [26]; the small enhancement by *ca.* 1.7 Hz may reflect the increase of the electronegativity of R in H_3C-R from 2.1 (R = H) to *ca.* 2.5 (R = C(sp^2)) [27]. Since the correlation between ^1J(C,H) and the charge has been set up [25], the precision of ^{13}C NMR measurement improved to such an extent that the impact of a charge on the N atom in N-CH_3 compounds upon ^1J(C,H), Δ^1J = *ca.* 10 Hz for a full charge, is larger by *ca.* two powers of ten with respect to the reliability of recorded coupling constants (as for the intended purpose only differences between recorded *J* values are required, the accuracy of the *absolute* figures is of no importance). We therefore chose ^1J(C,H) of the Me_2N groups of DAN compounds as an indicator of positive charge (complete or partial) at the N atom.

Results and Discussion

$^1J(^{13}C,{}^1H)$ *in reference compounds*

In dimethylaniline (**5a**), the one-bond coupling is ^1J(C,H) = 135.8 Hz (see Table 1). By π-electron withdrawal, the N atom acquires partial immonium character which raises ^1J(C,H) only very slightly, by $\Delta^1J = 0.6$ Hz in 4-dimethylamino-pyridine (**5b**) and by 1.3 Hz in 4-nitro-dimethylaniline (**5c**). Interestingly, this small enhancement is paralleled neither by a ^{13}C nor by a uniform ^1H downfield shift of the signals: $\Delta\delta(\mathrm{N}(CH_3)_2) = -1.59$ ppm (**5a**/**b**), -0.32 ppm (**5a**/**c**) (hence, a small and a negligible *high*field shift, respectively); $\Delta\delta(\mathrm{N}(CH_3)_2) = -0.01$ ppm (**5a**/**b**), $+0.12$ ppm (**5a**/**c**). In the naphthalenes **1a-c**, the adjacent *peri* position is unsubstituted. ^1J(C,H) = 134.9 – 135.7 Hz matches the coupling constant of **5a** well. Compound **1d** (with two non-equivalent Me groups within each DAN group as a consequence of hindered rotation; ^1J(C,H) = 133.6 and 134.5 Hz) shows that replacement of *peri*-H by a non-electrophilic C(sp^2) atom within a bulky substituent has an insignificant effect in spite of a slight enhancement of the substituent's electronegativity (the difference between the two Me groups, $\Delta^1J = 0.9$ Hz, is greater than 134.5 Hz *vs.* 134.9 Hz of **1a**). In **1e**, the *peri*-position is occupied by a C(sp^3) atom; again the bulky substituent hinders rotation and renders the Me groups non-equivalent. ^1J(C,H) = 135.6 and 135.7 Hz are unconspicuous. Introduction of a more electronegative *peri*-substituent, *viz.* Me_2N in **1f**, does not increase ^1J(C,H) either. If, on the other hand, a full positive charge is placed upon the N atom by intermolecular (**1g**: ^1J(C,H) = 145.0 Hz) or intramolecular quaternization (**1h**: ^1J(C,H) = 146.2 Hz), ^1J(C,H) rises by



Scheme 2. Alkylation and competing protonation of DAN-phosphines **2a**.

$\Delta^1J = 10-11$ Hz and reaches the values of Me_3N^+–R (R = O^-, OH, H, Me) (*vide supra*).

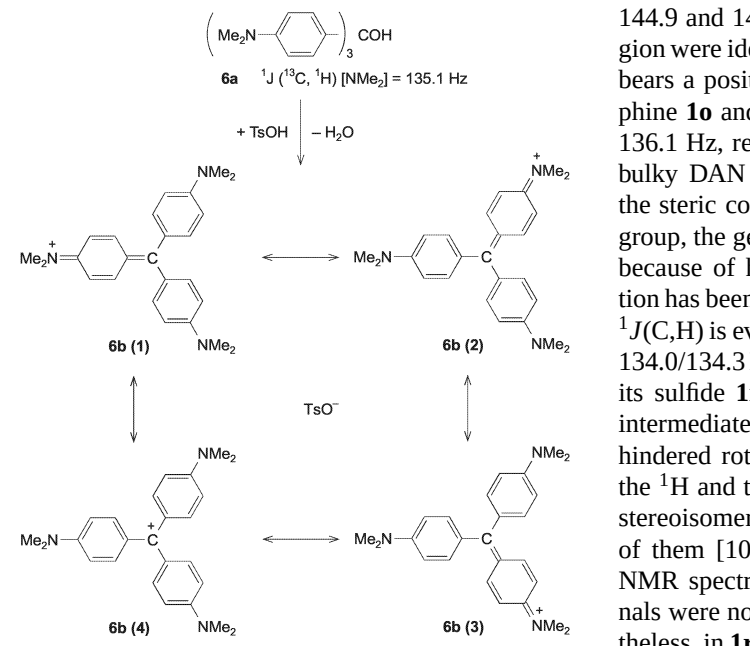
In view of the envisaged study of DAN-P compounds with respect to N→P interactions, it seemed desirable to replace N-quaternization by N-protonation (see Scheme 2), because H and P happen to have the same electronegativity, 2.1 [27]. In addition, an attractive interaction between Me_2N as a donor and an electrophilic *peri*-substituent would *reduce* the steric congestion in the *peri* space whereas N-quaternization of neutral DAN compounds *enhances* steric interaction between the *peri*-substituents. It was therefore advisable to use hydrogen as the smallest additional N-substituent possible. (We had earlier shown that in *p*DSN's the H atom of an isopropyl group and the N-lone pair of a Me_2N group are similar in their steric demand [28]). Finally no ammonium derivative of **1a**,**o** is available by quaternization which occurs at the Ph_2P group [19], whereas protonation takes place at the N atom of **1a** to yield **1j** [23].

For the protonations, *p*-toluenesulfonic acid (TsOH) offered several advantages. Except in **1f** (the *proton sponge*), the Me_2N group of DAN compounds is only moderately basic. To ensure virtually complete N-protonation, it was therefore necessary to use an excess of a strong acid. TsOH permitted to monitor its amount by integration (Me_2N of the DAN compound *vs*. Me of TsOH) in the ^{1}H NMR spectra. Except for **1f**/**n**, N-protonation remains kinetically unstable so that **1n** is the only case where $^2J(C–N^+–H)$ coupling was observed. The always well resolved Me(TsOH) signals in the ^{1}H-coupled ^{13}C NMR spectra (tq because of ^1J(C,H)[q] and ^3J(*C*-C(4)-C(3,5)-*H*(3,5)[t]) were a welcome check of the quality of the spectrum even in cases when the Me_2N section was not well resolved due to partially hindered rotations.

Not surprisingly, **1j**-**l** and **5d** likewise exhibited ^1J(C,H) couplings in the 144–146 Hz region (*cf.* Table 1). Similarly, bis-protonation of **1d** led to ^1J(C,H) = 145.3 Hz in **1m**. Interestingly, the high rotational barrier which rendered the Me groups non-equivalent in **1d**, was considerably lowered by N-protonation, and with respect to the ^{13}C NMR signal positions, only the highfield signal of **1d** was affected.

1f undergoes only mono-protonation [29]. In the cation **1n**, the two Me_2N groups are NMR-spectroscopically equivalent, so that both N atoms share one positive charge. Correspondingly, N-protonation (**1f**→**1n**) raises ^1J(C,H) by only $\Delta^1J =$ 6.2 Hz. It is, however, noteworthy that the enhancement amounts to 62–63% of the impact of N-protonation upon Δ^1J in **1a**–**c**→**1j**–**l** and thus exceeds 50% as anticipated for the effect of half of a positive charge. Additional experiments were performed to provide further insight (Scheme 3). 1.3 equivs of TsOH added to **5a** generated the salt **5d** and raised ^1J(C,H) by $\Delta^1J = 8.8$ Hz. A sub-stoichiometric amount of TsOH led to an averaged spectrum of **5a** and **5d**. In view of the moderate basicity of **5a**, the quantity of added TsOH (0.33 equivs) should leave *more* than 67% of the base unprotonated. Hence, *less* than 33% of **5d** account for an enhancement of ^1J(C,H) by 2.4 Hz (28%). The result is compatible with a linear dependence of ^1J(C,H) on the charge at N [30]. In an analogous experiment with **1a**, 0.74 equivs of TsOH caused ^1J(C,H) to rise by $\Delta^1J = 7.8$ Hz (78%). As *less* than 74% of the base should have been protonated, the enhancement of ^1J(C,H) seems somewhat overproportional.

Additional information about the impact of partial charges upon ^1J(C,H) was provided by crystal violet. The carbinol base, $(4\text{-}Me_2N\text{-}C_6H_4)_3C\text{-}OH$ (**6a**), is a *para*-substituted dimethylaniline in which the *para*-substituent, $C(sp^3)(OH)Ar_2$, is virtually devoid of electron-donating or -attracting properties. While the $N(^{13}CH_3)_2$ signal is at slightly higher field than in **1a**–**c**, ^1J(C,H) = 135.1 Hz complies well. TsOH creates the salt $[(4\text{-}Me_2N\text{-}C_6H_4)_3C]^+$ TsO^-(**6b**). If the positive charge is distributed exclusively among the three N atoms (Scheme 4, formulae **6b**(**1**–**3**)), each of them bears one third of a full charge. In case of a linear dependence of ^1J(C,H) on the charge at N, Δ^1J(C,H) = *ca*. 3.5 Hz would be anticipated. The observed values, ^1J(C,H) = 138.3 Hz, hence Δ^1J(C,H) = 3.2 Hz, match well. However, it remains undecided whether under the reaction conditions the equilibrium **6b**+H_2O⇌**6a**+TsOH was *completely* on the left side, or whether the spectra represent an average of the contributions of **6a** and **6b**. In addition, it is not known to what extent the formal carbenium center (*cf.* Scheme 4, formula **6b(4)**) has a share of the charge. The observed increase of 3.2 Hz may therefore account for *less* than



Ar	n	m(1)	m(1) + m(2)	$\Delta^1J(^{13}C,^1H)$ [Hz]
1a, j 4-$Ph_2PC_{10}H_6$	4	3	6.8	1) 7.8, 2) 2.2 (**1a** → **1j**: 10.0)
5a, d Ph	3	1	4	1) 2.4, 2) 6.4 (**5a** → **5d**: 8.8)

Scheme 3. The impact of partial and complete N-protonation upon $^1J(^{13}C,^1H)[NMe_2]$ of the amines Ar-NMe_2.

Scheme 4. The impact of one positive charge upon $^1J(^{13}C,^1H)[NMe_2]$ of three identical 4-Me_2N groups in crystal violet.

one third of a charge per N atom and therefore again reflect an overproportional increase of ^1J(C,H).

The pertinent data permit to conclude that ^1J(C,H) responds *at least* linearly to an increase of positive charge at the N atom and that therefore even a partial charge cannot remain undetected.

$^1J(^{13}C,^1H)$ *in DAN-P compounds*

In the series of DAN-P compounds, **1i** is the only case where a N–P bond has been firmly established [8]. Poor solubility in all common solvents, additional $^2J(H_3C–N–P)$ couplings and considerable overlap of the multiplets resulted in a complex ^{1}H-coupled ^{13}C NMR spectrum which resisted complete analysis. In the Me_2N part, four intersignal distances between 144.9 and 146.4 Hz and none in the 134 – 137 Hz region were identified. It is thus indicated that the N atom bears a positive charge. On the other hand, the phosphine **1o** and its oxide **1q** exhibit ^1J(C,H)=135.1 and 136.1 Hz, respectively. In the phosphine **1s**, the *three* bulky DAN groups attached to the P atom increase the steric congestion so much that within each Me_2N group, the geminal Me groups become non-equivalent because of hindered rotation. Though N→P interaction has been claimed for all three N atoms [12, 13, 17], ^1J(C,H) is even a little (though insignificantly) smaller, 134.0/134.3 Hz. In the phosphine $(DAN)_2PPh$ [10] and its sulfide **1r**, steric hindrance around the P atom is intermediate between that in **1o**,**q** and in **1s**. Partially hindered rotations lead to signal broadening both in the ^{1}H and the ^{13}C NMR spectra and give rise to two stereoisomers with four different Me groups in each of them [10]. The consequence are ^{1}H-coupled ^{13}C NMR spectra whose broadened and overlapping signals were not amenable to a stringent analysis. Nevertheless, in **1r** eight intersignal distances between 134.0 and 136.1 Hz could be identified, and none in the 144 to 146 Hz region. For contrast, N-protonation of **1q** raised ^1J(C,H) by 8.4 Hz to 144.5 Hz in **1u**, and in the complex spectrum of **1v** (= N-protonated **1r**), four intersignal distances between 142.0 and 147.7 Hz were identified.

In the phosphines $(DAN)_nPPh_{3-n}$, $n = 1-3$, the P atom is remarkably basic so that P-protonation supersedes N-protonation (*cf.* Scheme 2) [23]. Thereby non-quaternary DAN-phosphonium salts **2b** are formed in which the conditions for dative N→P interactions should be better than in the phosphines **2a** (because of the increased effective electronegativity of the P atom [31]) and better than in corresponding *quaternary* phosphonium salts **2c** [22], for which such interactions have been claimed [18] (because of smaller steric opposition against the required approach of the functional groups). In fact, P-protonation of **1o**,**s** raises ^1J(C,H) slightly (**1o**→**1p**: $\Delta^1J = 2.0$ Hz, equal with the increase from **6a** to **5c**; **1s**→**1t**: $\Delta^1J = 1.9$ and

1.3 Hz), but ^1J(C,H) remains in the 134 – 137 Hz region. For a rationalization, it seems unwarranted to invoke dative N→P$^+$–H interaction. It suffices to resort to a through space effect of the positive charge at the P atom in the immediate vicinity of the Me_2N group within the congested *peri* space. It is noteworthy that the *positions* of the ^1H_3C and $H_3{}^{13}C$ signals are scarcely affected (**1o**→**1p**: $\Delta\delta(^1H) = +0.05$ ppm, $\Delta\delta(^{13}C) = -0.36$ ppm [!]; **1s**→**1t**: $\Delta\delta(^1H) = -0.04$ [!] and +0.05 ppm, $\Delta\delta(^{13}C) = +0.88$ and −0.15 ppm [!]).

Other parameters

The three-bond coupling ^{13}C–N–C–^1H between the geminal Me groups of Me_2N is consistently significantly smaller whenever the lone pair at the N atom is engaged in an additional σ-bond. None of the DAN-P compounds exhibits this decrease (*cf.* Table 1).

In all DAN compounds, in **5a** – **c** and in **6a**,**b**, the C(sp^2) atom bearing the Me_2N group gave an isolated ^{13}C NMR signal at low field (*cf.* Table 1). Whenever the N atom had ammonium character (hence, when engagement of the N-lone pair in a σ-bond precluded π-conjugation with the aromatic system), there was no such isolated low field signal (for the ammonium compounds, the ^{13}C signals at the lowest field are listed in Table 1; they are invariably close to other signals, and their assignment remains open). Comparison of the data clearly shows that the spectra of all DAN-P compounds, including the DAN-P$^+$–H salts **2b**, exhibit this signal and that the (DAN-H$^+$)-P compounds **1u**,**v** do not. We take this as evidence that in none of the DAN-P compounds π-conjugation of the Me_2N group is reduced by N→P interaction.

Conclusion

^1J(C,H) values of Me_2N groups proved a valuable tool for the investigation of the charge distribution in Me_2N-substituted *p*DSN's. In DAN-phosphines, phosphine chalkogenides and non-quaternary phosphonium salts, the ^1J(C,H) data clearly show that there is no dative N→P interaction. Bonding in these compounds is adequately described by their Lewis octet formulae. While its nucleophilicity enables a Me_2N group to engage in bond formation with a suitable adjacent *peri* substituent (**1h**,**i**), the electrophilicity of Ar_2P, $Ar_2(O)P$, $Ar_2(S)P$ and even $Ar_2(H)P^+$ groups is insufficient to force the naphthalene skeleton into the distortion which is required for establishing a *peri*-N–P bond. The recent statement that *"the developing chemistry of phosphorus is renowned for 'breaking the rules' that are well established in organic chemistry"* [2] does not apply to the phosphorus in DAN-phosphines and their derivatives which fully complies with Lewis' *octet rule* (rule 1; see Introduction): To the present state of our knowledge, as nitrogen in amines, neutral phosphorus in phosphines cannot exceed tricovalency.

Experimental Section

The elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

*1-Dimethylamino-8-[(hydroxy)(phenyl)methyl]naphthalene (**1e**)*

A commercial 1.6 M solution of *n*-butyllithium in *n*-hexane (54 ml) was added to 1-dimethylaminonaphthalene (10.0 ml, 86 mmol) in anhydrous diethyl ether (30 ml). The mixture was stirred under argon for 5 d; then benzaldehyde (8.7 ml, 86 mmol) was added slowly. After hydrolytic workup (10 ml of water, 30 ml of 2N HCl) and recrystallization from ethanol, 11.3 g (47%) of DAN-C(H)(Ph)(OH) were isolated, m. p. 107 – 108 °C. – ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 2.31$ and 2.74 (2 s, 3 + 3 H, $N(CH_3)_2$), 6.35 (d, $^3J = 7.7$ Hz, 1 H, (HO)C-*H*), 7.19 – 7.80 (m, 12 H, arom. H + OH). ($C_2D_2Cl_4$, 114 °C): $\delta = 2.54$ (s, 6 H, $N(CH_3)_2$). – ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 46.30$, 47.72 ($N(CH_3)_2$), 76.37 (C-OH), 120.45 – 145.06 (arom. C), 150.03 (Me_2N-C). – $C_{19}H_{19}NO$ (277.4): calcd. C 82.27, H 6.90, N 5.05; found C 82.02, H 6.92, N 5.10.

1,1-Dimethyl-2-phenyl-1-azonia-acenaphthene salts

A mixture of **1e** (1.10 g, 4.0 mmol), *p*-toluenesulfonyl chloride (600 mg, 3.15 mmol) and 10 ml of pyridine was stirred for 4 h at 0 °C, then poured on ice and made alkaline by addition of ammonia. 300 mg of unreacted carbinol were filtered off. Upon partial evaporation of the filtrate, 640 mg (51%) of **1h** precipitated. The salt had no m. p. and decomposed when heated to 220 °C. From a solution in methanol, the corresponding tetraphenylborate crystallized after addition of a methanol solution of $NaBPh_4$: colourless crystals of m. p. 166 – 168 °C, $C_{43}H_{38}BN$ (579.6): calcd. C 89.11, H 6.61, N 2.42; found C 88.58, H 6.63, N 2.39.

All other compounds were known and were prepared according to published procedures except **1f** and **5a**,**b** which were commercial products.

NMR measurements

Unless otherwise stated, the ^1H and ^{13}C NMR spectra were recorded at room temperature with a Bruker ARX300

Table 3. Individual coupling constants $^{1,3}J(^{13}C,^{1}H)$ [Hz] in $C_6H_5NMe_2$ (**5a**) and $C_6H_5N^+(H)Me_2$ TsO^- (**5d**).

	Amine (**5a**)		**5a** + **5d**: Amine + cation,		**5a** + **5d**: Anion,		**5d**: Cation,		**5d**: Anion,	
	NMe_2: ^1J	NMe_2: ^3J	NMe_2: ^1J	NMe_2: ^3J	Ar-Me: ^1J	Ar-Me: ^3J	NMe_2: ^1J	NMe_2: ^3J	Ar-Me: ^1J	Ar-Me: ^3J
$\Delta\delta(B^{A(1)}(1) - B^{A(2)}(1))$	135.10		138.23		126.67		144.70		126.82	
$\Delta\delta(B^{A(1)}(1) - B^{A(1)}(2))$		4.09		3.95		4.43		3.88		4.42
$\Delta\delta(B^{A(1)}(2) - B^{A(2)}(2))$	135.06		138.24		126.65		144.63		126.74	
$\Delta\delta(B^{A(1)}(2) - B^{A(1)}(3))$		4.03		3.95		4.41		3.74		4.67
$\Delta\delta(B^{A(1)}(3) - B^{A(2)}(3))$	135.09		138.26		126.66		144.64		126.53	
$\Delta\delta(B^{A(1)}(3) - B^{A(1)}(4))$		4.31		4.01		–		3.69		–
$\Delta\delta(B^{A(1)}(4) - B^{A(2)}(4))$	134.82		138.22		–		144.68		–	
$\Delta\delta(B^{A(2)}(1) - B^{A(2)}(2))$		4.06		3.96		4.41		3.81		4.34
$\Delta\delta(B^{A(2)}(1) - B^{A(3)}(1))$	135.11		138.23		126.65		144.72		126.67	
$\Delta\delta(B^{A(2)}(2) - B^{A(2)}(3))$		4.06		3.97		4.42		3.75		4.43
$\Delta\delta(B^{A(2)}(2) - B^{A(3)}(2))$	135.10		138.24		126.66		144.64		126.74	
$\Delta\delta(B^{A(2)}(3) - B^{A(2)}(4))$		4.03		3.97		–		3.73		–
$\Delta\delta(B^{A(2)}(3) - B^{A(3)}(3))$	135.08		138.24		126.70		144.65		126.72	
$\Delta\delta(B^{A(3)}(1) - B^{A(3)}(2))$		4.05		3.97		4.42		3.73		4.41
$\Delta\delta(B^{A(2)}(4) - B^{A(3)}(4))$	135.05		138.23		–		144.59		–	
$\Delta\delta(B^{A(3)}(2) - B^{A(3)}(3))$		4.05		3.97		4.46		3.76		4.41
$\Delta\delta(B^{A(3)}(1) - B^{A(4)}(1))$	135.00		138.23		126.67		144.89		127.09	
$\Delta\delta(B^{A(3)}(3) - B^{A(3)}(4))$		4.00		3.96		–		3.67		–
$\Delta\delta(B^{A(3)}(2) - B^{A(4)}(2))$	135.07		138.23		126.66		144.49		126.68	
$\Delta\delta(B^{A(4)}(1) - B^{A(4)}(2))$		4.12		3.97		4.41		3.33		4.00
$\Delta\delta(B^{A(3)}(3) - B^{A(4)}(3))$	135.09		138.23		126.74		144.66		126.57	
$\Delta\delta(B^{A(4)}(2) - B^{A(4)}(3))$		4.06		3.97		4.54		3.93		4.30
$\Delta\delta(B^{A(3)}(4) - B^{A(4)}(4))$	135.34		138.24		–		144.47		–	
$\Delta\delta(B^{A(4)}(3) - B^{A(4)}(4))$		4.25		3.97		–		3.48		–
average	135.08	4.09	138.24	3.97	126.66	4.44	144.65	3.71	126.73	4.37

spectrometer at 300.130 and 75.468 MHz, respectively. CD_2Cl_2 was used as a solvent at concentrations of *ca.* 80 mg/ml whereever permitted by the solubility. The $\delta(^{13}C)$ values were obtained from the ^1H-decoupled ^{13}C NMR spectra, the J(C,H) values from the ^1H-coupled ^{13}C NMR spectra. As representative specimens for all spectra which did not exhibit line broadening due to partially hindered rotations, the full set of coupling constants (as printed out by the spectrometer) of $PhNMe_2$ (**5a**, neutral, with substoichiometric and with superstoichiometric amounts of TsOH) is presented in Table 3. In the ^1H-coupled ^{13}C NMR spectra, the N-CH_3 part consists of a well resolved quartet of quartets, caused by ^1J(C–H) coupling of ^{13}C with three protons within each methyl group and ^3J(*C*–N–C–*H*) coupling of ^{13}C of one methyl group with the three protons of the other methyl group. Each spectrum thus contains ^1J and ^3J in 12 independent recordings each. The spectrum of $PhN^+(H)Me_2$ TsO^- (**5d**) exhibits the additional signals of the methyl group of the anion as an equally well resolved quartet of triplets, caused by ^1J(C–H) coupling within the methyl group and ^3J(*C*–C–C –*H*) coupling between the methyl C atom and the 3,5-H atoms, so that ^1J is independently recorded 9 times and ^3J 8 times. In Table 3, the four signal groups representing the ^1J quartet are labeled A(n) ($n = 1, 2, 3, 4$, with decreasing frequency), and the four (in the anion: three) signals of each A(n) multiplet $B^{A(n)}(m)$ ($m = 1, 2, 3, (4)$). The J values are the differences of the pertinent $B^{A(n)}(m)$ data in Hz. In **1o**, the $^{1/3}J$ quartet of quartets was doubled by ^5J(P,C) coupling. Of the expected 32 signals, 24 were recorded in an equally well resolved spectrum, 8 of the less intensive ones being buried beneath the absorption of overlapping signals of higher intensity. Thus ^1J(C,H) was obtained in 18 independent recordings, ^3J(C,H) in 16 independent recordings (^5J(P,C) was also observed in **1s**, but restricted rotations led to a more complicated and less well resolved spectrum; *cf.* Table 1, note 38). In a number of spectra, only the more intensive "inner" signals of the A(n)-quadruplets were equally well resolved. The data in Table 1 were obtained by averaging all individual J values with subsequent round-off.

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[1] 10th Communication: G. P. Schiemenz, C. Näther, S. Pörksen, Z. Naturforsch. **58b**, 663 (2003).
[2] a) U. Lüning, Reaktivität, Reaktionswege, Mechanismen, Spektrum Akademischer Verlag, Heidelberg, Berlin (1997); b) U. Lüning, Christiana Albertina **55**, 73 (2002).
[3] P. Kilian, D. Philp, A. M. Z. Slawin, J. D. Woollins, Eur. J. Inorg. Chem. 249 (2003).
[4] *Rule of eight* in Lewis' original version: R. J. Gillespie, P. L. A. Popelier, Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities, Oxford University Press, New York, Oxford (2001).
[5] N. Burford, P. J. Ragogna, J. Chem. Soc., Dalton Trans. 4307 (2002).
[6] L. Landshoff, Ber. Dtsch. Chem. Ges. **11**, 638 (1878). Note that the product, $C_{10}H_7N^+Me_3\ I^-$, even engages in the reverse reaction fairly easily.
[7] H. W. W. Ehrlich, Acta Crystallogr. **10**, 699 (1957).
[8] G. P. Schiemenz, S. Pörksen, C. Näther, Z. Naturforsch. **55b**, 841 (2000).
[9] S. S. Batsanov, Izvest. Akad. Nauk, Ser. Khim. 24 (1995); Russ. Chem. Bull. **44**, 18 (1995).
[10] M. Chauhan, C. Chuit, R. J. P. Corriu, C. Reye, J.-P. Declercq, A. Dubourg, J. Organomet. Chem. **510**, 173 (1996).
[11] F. Carre, M. Chauhan, C. Chuit, R. J. P. Corriu, C. Reye, Phosphorus, Sulfur, Silicon Relat. Elem. **123**, 181 (1997).
[12] C. Chuit, C. Reye, Eur. J. Inorg. Chem. 1847 (1998). Recently, even a formal "forshortening" of 0.8% and 0.0% found for the intermolecular distances $d(\mathrm{Pd}\cdots\mathrm{NO_2})$ in two palladium complexes with a 4-nitroaryl group bound to the Pd atom has been attributed to a bonding orbital interaction between Pd as a *Lewis acid* and the N atom of the nitro group acting as a donor by means of its π-orbital: M. Q. Slagt, H. P. Dijkstra, A. McDonald, R. J. M. Klein Gebbink, M. Lutz, D. D. Ellis, A. M. Mills, A. L. Spek, G. van Koten, Organometallics **22**, 27 (2003). However, the deviation from Σr(vdW), as given by the authors with reference to A. Bondi, J. Phys. Chem. **68**, 441 (1964), is zero in one case and within the precision of van der Waals radii in the other (*cf.* lit. [4] and the van der Waals radii as given, *e. g.*, in: a) J. E. Huheey, Anorganische Chemie. Prinzipien von Struktur und Reaktivität, p.278 – 279, Walter de Gruyter, Berlin, New York (1988); b) F. A. Cotton, G. Wilkinson, P. L. Gaus, Grundlagen der Anorganischen Chemie, p. 97, VCH, Weinheim, New York, Basel, Cambridge (1990); c) lit. [9]). With $r(\mathrm{vdW}_{Pd})$ = 163 pm (as proposed by Bondi, *l.c.*, pp. 448 – 449 for *metals (in nonmetallic compounds)*), hence $\Sigma r(\mathrm{vdW_{N,Pd}})$ = 318 pm, the actual distances exceed Σr(vdW) by 20 – 21%. Hence, no dative interactions are indicated, while Coulomb attraction between the electropositive Pd and the electronegative N^+ is likely to account for the head-to-tail arrangement of the molecules.
[13] C. Chuit, R. J. P. Corriu, P. Monforte, C. Reye, J.-P. Declercq, A. Dubourg, Angew. Chem. **105**, 1529 (1993); Angew. Chem. Int. Ed. **32**, 1430 (1993).
[14] G. P. Schiemenz, B. Schiemenz, S. Petersen, C. Wolff, Chirality **10**, 180 (1998).
[15] *E. g.*, A. C. Cope, E. R. Trumbull, Org. Reactions **11**, 317 (1960); R. F. Hudson, Structure and Mechanism in Organo-Phosphorus Chemistry, pp. 67 – 68, Academic Press, London, New York (1965).
[16] C. Chuit, R. J. P. Corriu, P. Monforte, C. Reye, J.-P. Declercq, A. Dubourg, J. Organomet. Chem. **511**, 171 (1996).
[17] F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reye, Inorg. Chim. Acta **250**, 21 (1996); A. Chandrasekaran, N. V. Timosheva, R. O. Day, R. R. Holmes, Inorg. Chem. **39**, 1338 (2000).
[18] F. H. Carré, C. Chuit, R. J. P. Corriu, W. E. Douglas, D. M. H. Guy, C. Reye, Eur. J. Inorg. Chem. 647 (2000).
[19] G. P. Schiemenz, E. Papageorgiou, Phosphorus Sulfur **13**, 41 (1982).
[20] G. P. Schiemenz, R. Bukowski, L. Eckholtz, B. Varnskühler, Z. Naturforsch. **55b**, 12 (2000).
[21] G. Dyker, M. Hagel, G. Henkel, M. Köckerling, C. Näther, S. Petersen, G. P. Schiemenz, Z. Naturforsch. **56b**, 1109 (2001).
[22] G. P. Schiemenz, S. Pörksen, P. M. Dominiak, K. Wozniak, Z. Naturforsch. **57b**, 8 (2002).
[23] G. P. Schiemenz, C. Näther, S. Pörksen, Z. Naturforsch. **58b**, 59 (2003).
[24] G. A. Landrum, N. Goldberg, R. Hoffmann, J. Chem. Soc., Dalton Trans. 3605 (1997).
[25] P. Haake, W. B. Miller, D. A. Tyssee, J. Am. Chem. Soc. **86**, 3577 (1964).
[26] H.-O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR-Spektroskopie, p. 447, Georg Thieme Verlag, Stuttgart, New York (1984).
[27] L. Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals, 2*nd* ed., p. 64, Cornell University Press, Ithaca NY, London, Oxford (1945); 3*rd* ed., p. 90, 93, *ibid.* (1960).
[28] G. P. Schiemenz, C. Näther, Z. Naturforsch. **57b**, 309 (2002).
[29] a) H. A. Staab, T. Saupe, Angew. Chem. **100**, 895 (1988); Angew. Chem. Int. Ed. **27**, 865 (1988); b) R. W. Alder, Chem. Rev. **89**, 1215 (1989).
[30] *Cf.* Kalinowski *et al.* [26], pp. 446-448.
[31] *Cf.* Pauling [27], 2*nd* ed., pp. 65-66.
[32] D. Bright, I. E. Maxwell, J. de Boer, J. Chem. Soc., Perkin Trans. 2, 2101 (1973).

[33] R. L. Clough, W. J. Kung, R. E. Marsh, J. D. Roberts, J. Org. Chem. **41**, 3603 (1976).
[34] J.-B. Robert, J. S. Sherfinski, R. E. Marsh, J. D. Roberts, J. Org. Chem. **39**, 1152 (1974).
[35] E. Wehman, G. van Koten, M. Knotter, H. Spelten, D. Hejdenrijk, A. N. S. Mak, C. H. Stam, J. Organomet. Chem. **325**, 293 (1987).
[36] R. W. Alder, P. S. Bowman, W. R. S. Steele, D. R. Winterman, J. Chem. Soc., Chem. Commun. 723 (1968).
[37] a) A. Groll, Ber. Dtsch. Chem. Ges. **19**, 198 (1886); b) E. Noelting, E. Fourneaux, *ibid*. **30**, 2930 (1897).
[38] T. Wieland, W. Sucrow (eds): Gattermann-Wieland, Die Praxis des organischen Chemikers, 43rd ed., pp. 582-583, Walter de Gruyter, Berlin, New York (1982).
[39] B. Brycki, B. Brzezinski, E. Grech, Z. Malarski, L. Sobczyk, Magn. Reson. Chem. **29**, 558 (1991).
[40] G. P. Schiemenz, C. Näther, S. Pörksen [1], ref. 32.
[41] D. Hellwinkel, W. Lindner, H.-J. Wilfinger, Chem. Ber. **107**, 1428 (1974).