

peri-Interactions in Naphthalenes, 6 [1]. On Hypercoordination of Phosphorus in 8-Dialkylamino-naphth-1-yl Phosphonium Salts

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Z. Naturforsch. **57 b**, 8–18 (2002); received August 2, 2001

peri-Naphthalenes, Hypercoordination, Steric Effects

Under favourable conditions, the phosphorus centres in tetraorganophosphonium cations are sufficiently electrophilic to become hypercoordinate by reaction with *strong* nucleophiles. However, as a *peri* substituent at the naphthalene system, such a centre proved to be unable to induce the nitrogen of a *peri*-bound dialkylamino group to bond formation. The distortion of the naphthalene skeleton revealed by X-ray structure determination of four 8-dialkylamino-naphth-1-yl phosphonium salts does not exhibit the criteria of N-P bond formation but rather those of intersubstituent repulsion.

Introduction

Substituent interactions in *peri*-substituted naphthalenes and related systems with rigid geometries presently attract much interest [2]. The consequences of steric hindrance as well as the possibilities of electronic interactions (including, *e. g.*, through space coupling of NMR-active nuclei [3]) have been investigated. A special aspect in this area is the bond forming process between nucleophilic and electrophilic substituents [4].

In 8-dialkylamino-naphth-1-yl phosphorus (DAN-P) compounds (Figs 2, 5), the phosphorus atom could conceivably become hypercoordinate as a consequence of electron donation from nitrogen to phosphorus. Based on various concepts of interpretation contrasting conclusions have been drawn [5 - 20]. We developed what we believe to be safe criteria to extract information about bond formation between *peri* substituents in 1,8-disubstituted naphthalenes from X-ray diffraction data [14, 18 - 21].

In a naphthalene molecule of ideal geometry (planar, all angles 120°), the distance between the carbon atoms 1 and 8 (and 4 and 5) is 2.47 Å [20, 21]. This would also be the distance between two equal *peri* substituents, d(S(1)...S(2)) (Fig. 1, 1). In cases of unequal *peri* substituents (2), the ideal *peri* distance can be a little longer, *e. g.* d(N...P) = 2.50 Å [18 - 20], d(N...Si) = 2.51 Å [20, 21], d(N...Te) = 2.55 Å [20]. On the one hand, all these distances are

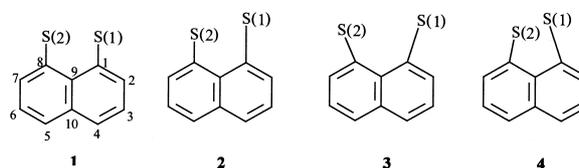


Fig. 1. Geometric conditions in *peri*-substituted naphthalenes.

too short to accommodate any *peri* substituents except hydrogen. Steric hindrance enforces deformations of the naphthalene skeleton. These can be in-plane and/or out-of-plane. Frequently, the in-plane deformation is predominating [22 - 24]: the sum of the three bay angles: S(1)-C(1)-C(9), C(1)-C(9)-C(8) and S(2)-C(8)-C(9) will exceed 360°, the sum of the three angles minus 360° being the splay angle (3) [19, 20]. In such cases, the distance between the *peri*-bound atoms S(1) and S(2) is longer than *ca.* 2.50 Å [25], usually about 2.65 to *ca.* 3.00 Å. Such distances, as well as positive splay angles, indicate safely steric hindrance [20]. Out-of-plane deformations, *viz.* one *peri*-substituent above, the other one below the average naphthalene plane, provide additional evidence [26].

On the other hand, covalent bonds (including “hypervalent” ones) are quite resistant to stretching [1, 20], and the ideal *peri*-distance of *ca.* 2.47 - 2.55 Å is much too long for any appreciable bonding between atoms of second and third period elements [18, 20]. If a bond forms

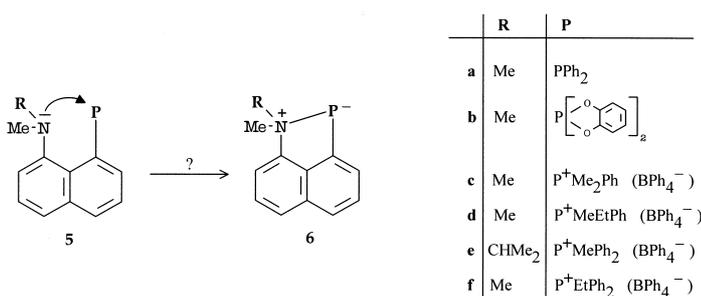


Fig. 2. Potential N→P interaction in DAN-phosphorus compounds.

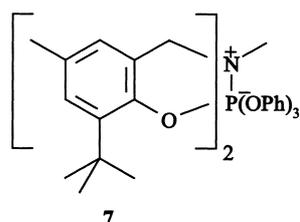


Fig. 3. Example of an unstrained system with hypercoordinate P-N bond [16, 17, 32].

between the *peri* substituents, it will be much shorter and, consequently, force the naphthalene skeleton into distortion [1, 27 - 31]. In this case, the sum of the three bay angles is $< 360^\circ$, *i. e.* the splay angle is negative (*cf.* 4). In hydrocarbon chemistry, examples are provided by 1,8-dimethyl-naphthalene (steric repulsion, $d(\text{H}_3\text{C}\dots\text{CH}_3) = 2.93 \text{ \AA}$, splay angle $+14.7^\circ$ [22]) and acenaphthene ($d(\text{H}_2\text{C}-\text{CH}_2) = 1.54 \text{ \AA}$ (as in ethane), splay angle -31.1° [27]). In the realm of DAN-P compounds, analogous behaviour is met on the one hand in DAN-phosphines (8-Me₂NC₁₀H₆-PPh₂ (5a): $d(\text{N}\dots\text{P}) = 2.706 \text{ \AA}$, splay angle $+5.3^\circ$ [11, 13, 16, 17, 32]: repulsion), on the other hand in a compound with hexacoordinate phosphorus, 1,1-dimethyl-2,2-bis(1,2-phenylenedioxy)-1-azonia-2 λ^6 -phosphata-acenaphthene (6b) ($d(\text{N}\dots\text{P}) = 2.132 \text{ \AA}$, splay angle -11.5° [20]).

Whereas DAN-phosphines with three P-C bonds and an electron pair at phosphorus such as 5a and 10 are bad candidates for hypercoordination, the substitution pattern at the P atom of 5b provides optimal conditions for the formation of an extra bond: Four oxygen atoms incorporated in two five-membered rings greatly enhance the electrophilicity of the phosphorus atom [33]. The N-P bond formed in the process 5b → 6b is obviously sufficiently strong to pay the energetic bill of the distortion of the naphthalene system. In a more flexible structure, 7, in which no such energetic drawback has to be

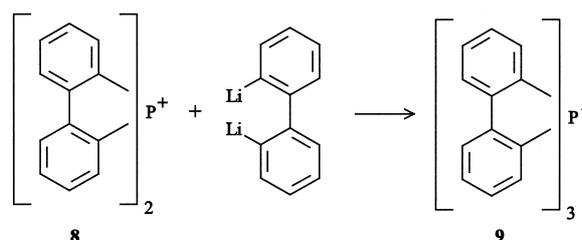


Fig. 4. Hypercoordination of phosphonium phosphorus by action of a strong nucleophile [34].

overcome, the N-P bond has the same length ($d(\text{N}\dots\text{P}) = 2.143 \text{ \AA}$ [16, 17, 34]), *i. e.*, if formed in DAN-P compounds, the N-P bond will not yield to the stress imposed by the rigid C₁₀ skeleton and stretch, but rather keep its length and force the C₁₀ skeleton into distortion.

The question then arises to what extent the electrophilicity of phosphorus, exceedingly low in phosphines, has to be enhanced as to permit N→P bond formation. In contrast to triphenylphosphine, the tetraphenylphosphonium cation is sufficiently electrophilic to react with *strong* nucleophiles, *e. g.* with phenyl lithium to give pentaphenylphosphorane [35]. As in the case of 6b, five-membered ring systems are favourable for hypercoordination so that the reaction of the spiro-phosphonium cation 8 with 2,2'-dilithiated biphenyl even yields tris(2,2'-biphenylene)phosphate (9) with hexacoordinate phosphorus [36]. On the other hand, the nitrogen atom of an aryl-dimethylamine is a comparatively poor nucleophile.

The X-ray data of DAN-phosphonium salts would thus permit a straightforward decision: When $d(\text{N}\dots\text{P})$ is considerably shorter than 2.50 \AA , *viz. ca.* $2.13 - 2.14 \text{ \AA}$, and the splay angle is negative, then there is a N-P bond, and the phosphorus is hypercoordinate. On the other hand, $d(\text{N}\dots\text{P}) > ca. 2.50 \text{ \AA}$, a positive splay angle and possibly out-of-plane de-

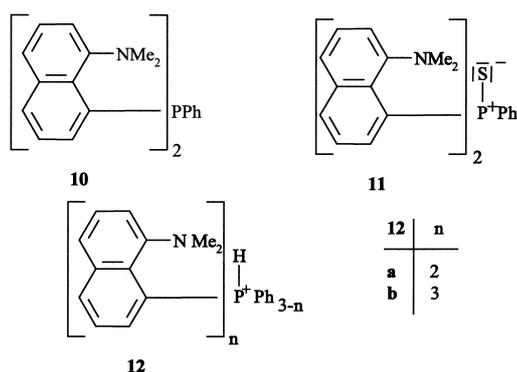


Fig. 5. Bis- and tris-(dimethylamino-naphthyl) phosphorus compounds.

formations would safely indicate steric repulsion and the absence of $N \rightarrow P$ bonding interaction [37].

The aim of our paper is to find out whether in 8-dialkylamino-naphth-1-yl phosphorus derivatives with a solely C-bound phosphorus atom, an onium character of the P atom enhances its electrophilicity sufficiently to enable it to form a hypercoordinate bond with the neighbouring nitrogen atom.

Results and Discussion

The general result obtained from three new DAN-phosphonium tetraphenylborates, **5c-e**, and a phosphonium salt from our previous study [7], **5f**, is clear-cut: $d(N \dots P)$ ranges from 2.891 (**5d**) to 2.958 Å (**5e**) and is thus *longer* than in the corresponding phosphine **5a**. The splay angles range from +5.8° (**5c**) to +7.6° (**5f**) and are likewise *larger* than those of **5a**. The non-bonding distances $C(1) \dots C(8)$, 2.50 - 2.54 Å, are somewhat *longer* than those in the ideal naphthalene molecule, and the opposite *peri* distances $C(4) \dots C(5)$, 2.39 - 2.465 Å, slightly (but consistently) *shorter*. The torsional angles $N-C(8) \dots C(1)-P$, between 25 and 32°, are a measure of a considerable out-of-plane deformation.

All data thus testify steric repulsion and are not compatible with $N \rightarrow P$ bonding. A first glimpse at the phosphonium substituents might suggest that steric hindrance should increase in the series $PMe_2Ph < PMeEtPh < PMePh_2 < PPh_3$, *i. e.* **5c** < **5d** < **5e** < **5f**. The splay angles follow, indeed, this order; however, they do not strictly corroborate this expectation, because the out-of-plane distortion does not regularly follow this trend (31.5, 25, 29, 25/31°). Likewise, the corresponding $d(N \dots P)$ values, equal to 2.941, 2.891, 2.958, 2.897/2.955 Å,

respectively, are not in this order. Closer inspection of the conformations adopted in the crystals reveals, in fact, a more complex situation. The two alkyl groups at nitrogen are not symmetrically positioned with respect to the naphthalene plane. One of the methyl groups of **5c, d, f** and the isopropyl group of **5e** is more or less in a perpendicular position, the (other) methyl group in a skew position in the anti-clinal (*ac*) sector [38] with respect to the $C(1) \dots C(8)$ connecting line. The *peri* space available for the substituents at phosphorus is thus unsymmetrically shaped above and below the C_{10} plane. In **5d**, the N-C bond of the nearly perpendicular methyl group and the P-CH₃ bond are parallel, and the other N-CH₃ and the P-C(Ph) bonds are nearly so, the ethyl group residing outside the *peri* space. This arrangement looks reasonable in terms of steric effects. Similarly, in **5e**, the smallest of the groups attached to phosphorus, CH₃, resides at the same side of the C_{10} plane as the larger group at N, CHMe₂, which deviates from orthogonality by 10° of inclination into the *ac* sector [38]. In **5f**, the P-C bonds adopt directions similar to those in **5d**, but the positions of the ethyl group and of one phenyl group are interconverted, the second phenyl group assuming the position of the methyl group of **5d**. Though, because of the similar steric demand of ethyl and phenyl, this arrangement could hardly be predicted, it is still in line with a stereochemical rationalization. On the other hand, in **5c** the two small groups at P share the less hindered face of the C_{10} plane, and the large group is close to the perpendicular N-CH₃ group. This arrangement is hard to understand from a steric point of view. We therefore restrict ourselves to the conclusion that the degree of steric hindrance is roughly the same in all four cations and that it is stronger than in the phosphine **5a**.

The unsymmetrical arrangement of the alkyl groups at N implies that the electron pair is neither in the C_{10} plane, nor does it point towards the P atom [39]. In fact, the angle between the electron pair and the P...N connecting line is: **5c**: 43.4°; **5d**: 47.7°; **5e**: 46.5°; **5f**: 44.4/44.9°, a fact which would be hard to reconcile with electron donation from N to P.

The alternative interpretation in favour of "a weak dative $N \rightarrow P$ bonding interaction" [40 - 42] would rest on two presuppositions which, in our opinion, are untenable: a) that the stretching of a N-P "hypercoordinate" bond from *ca.* 2.13 Å by *ca.* 0.80 Å is

Table 1. Selected most important structural parameters (distances in Å, angles in degrees).

Structural parameter	5c	5d	5e	5f**	5f**	DBAN-Br
N1-P1	2.939(2)	2.891(2)	2.959(2)	2.893(6)	2.953(6)	2.991(4)
P1-C1-C9	124.67(18)	125.57(16)	124.31(17)	124.9(6)	126.1(6)	122.8(4)
C1-C9-C8	124.6(2)	124.1(2)	125.5(2)	125.6(8)	122.8(8)	128.0(5)
N1-C8-C9	116.6(2)	116.7(2)	117.1(2)	116.8(8)	118.9(8)	118.6(4)
N1-C8-C1-P1	31.54(15)	-25.10(14)	29.43(15)	-25.5(5)	-31.2(5)	-22.6(3)
C1-C8	2.526(4)	2.531(3)	2.543(3)	2.507(12)	2.489(12)	2.559(7)
C4-C5	2.465(7)	2.460(4)	2.450(4)	2.398(15)	2.447(16)	2.443(10)
N1-C8	1.427(3)	1.430(3)	1.430(3)	1.420(9)	1.412(9)	1.413(6)
P1-C1	1.800(2)	1.804(2)	1.807(2)	1.791(7)	1.797(7)	1.908(6)
C81-N1-C8-C1	-147.3(2)	138.6(2)	-132.5(2)	141.4(6)	146.9(5)	153.1(4)
C82-N1-C8-C1	89.8(2)	-98.8(2)	99.87(18)	-96.8(5)	-89.2(5)	-73.5(4)
C21-P1-C1-C8	-75.06(13)	-49.69(13)	-76.47(17)	73.4(4)	75.2(4)	-
C31-P1-C1-C8	168.78(15)	81.05(19)	166.63(11)	-169.8(4)	-166.7(4)	-
C41-P1-C1-C8	54.53(16)	-163.87(17)	53.32(13)	-56.3(4)	-51.3(4)	-
2e(N1)*-N1-P1	43.4	47.7	46.5	44.0	44.4	59.6

* 2e(N1) = electron pair at N1; ** 2 independent molecules in the unit cell.

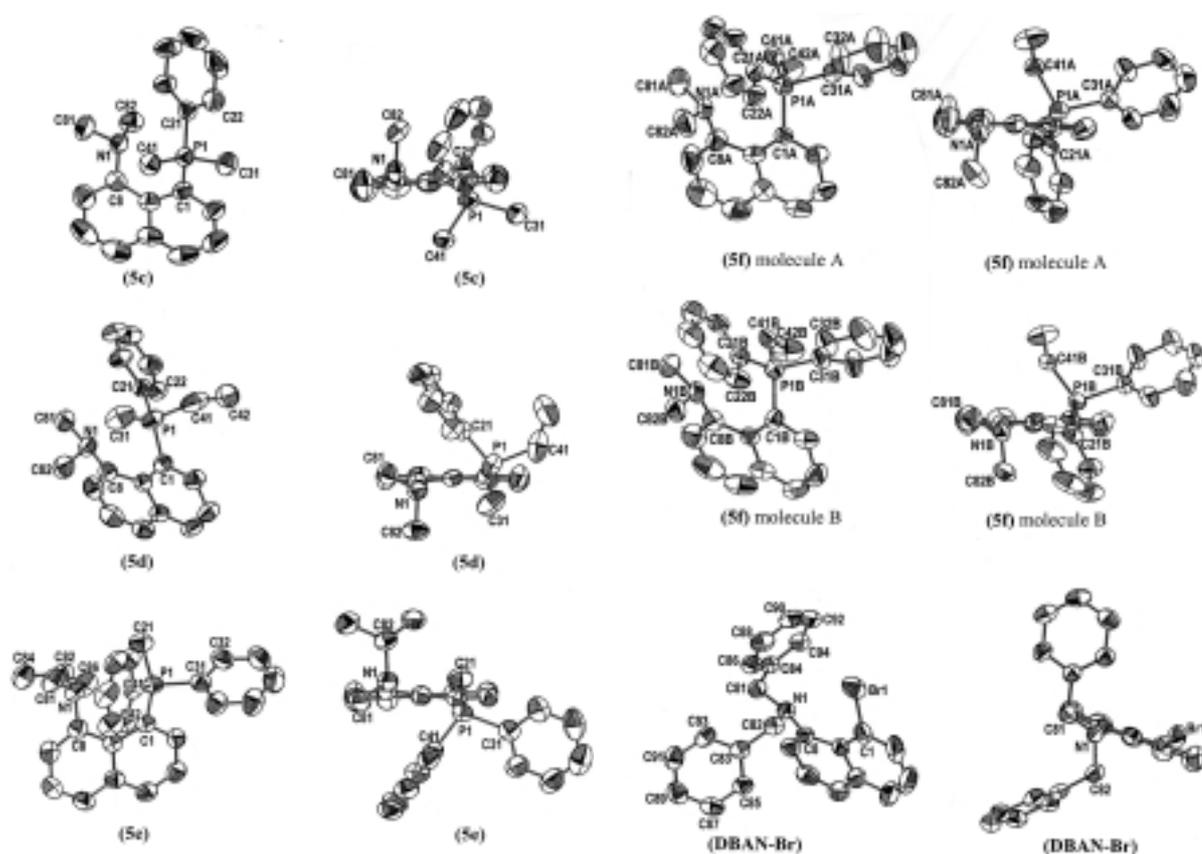


Fig. 6. ORTEP plots of the cations of **5c-f** and of **DBAN-Br** showing the labelling of relevant atoms. The projections on the right side of this figure show the molecules as seen along the C(9)-C(10) bond.

possible, b) that in systems whose geometry is defined by bond lengths and bond angles, interatomic distances shorter than the sum of the respective van der Waals radii, $\Sigma r(\text{vdW})$, testify any sort of covalent bonding [43]. Along the lines of this interpretation, the result would be paradoxical in so far as one would have to conclude that N→P bonding interaction is stronger in the phosphine **5a** (because the N...P distance is shorter) than in the compounds with positively charged phosphorus.

For comparison, we investigated 1-bromo-8-dibenzylamino-naphthalene (**DBAN-Br**) as a compound in which the second *peri* substituent is rotationally symmetric. Though hypercoordinate bromine is known (*e. g.*, in trihalide anions [41, 44]), a N→Br interaction seems unlikely, and it is, in fact, ruled out by the large angle between the electron pair at N and the N...Br connecting line (59.6°). Not surprisingly because of the large size of Br, the distance $d(\text{N...Br}) = 2.991 \text{ \AA}$ (*i. e.* much shorter than $\Sigma r(\text{vdW}) = 3.45 \text{ \AA}$ [45]) is even longer than in **5c-f**. Correspondingly, the splay angle, +9.4°, is larger than those found for the phosphonium salts. The out-of-plane deformation, however, is smaller (torsional angle N-C(8)...C(1)-Br 22.6°). The grossly analogous arrangement indicates a similar situation in bonding and steric effects and thus supports our conclusion concerning the phosphonium salts.

We therefore conclude that in the DAN-P compounds with four P-C bonds, a positive charge at phosphorus is insufficient to induce the *peri*-nitrogen atom to donate its electron pair into a N-P bond. The present X-ray data are thus in line with the conclusions which we earlier drew from ¹H and ³¹P NMR data [7].

In the (DAN)₂P and (DAN)₃P compounds, overcrowding in the *peri* space is even more pronounced so that such compounds need not necessarily show strictly analogous behaviour. However, a comparison between the phosphine **10** and its sulfide **11** [10] is revealing. The X-ray structural data have been interpreted in favour of a weak dative N→P bonding interaction [10] (see above). For both compounds, they exhibit the criteria of steric repulsion (**10**: $d(\text{N...P}) = 2.781, 2.792 \text{ \AA}$; splay angles 1.1°, 6.5°, respectively; **11**: $d(\text{N...P}) = 3.011, 3.009 \text{ \AA}$; splay angles 5.1°, 5.4°, respectively [10]). Phosphine sulfides are deprotonated mercapto-tri(organo)phosphonium salts [19] (*i. e.* the anions of very strong acids) so that the phosphine sulfide can aptly be described as a quaternary (DAN)₂ phosphonium cation in which one carbon atom has been replaced by a negatively charged sulfur atom without much change in electronegativity (*cf.* Pauling: C 2.5, S⁻ *ca.* 2.2 [46]). What would again be paradoxical in terms of hypercoordinative interaction, would then be straightforward in terms of steric hindrance: $d(\text{N...P})$ (**10**) < $d(\text{N...P})$ (**11**).

In the non-quaternary phosphonium cation **12a**, $d(\text{N...P}) = 2.70, 2.74 \text{ \AA}$ and splay angles of +4.7°, +7.0° have been found [12], *i. e.* again the criteria of steric repulsion. Since $d(\text{N...P})$ is more informative than the splay angles, one might suspect that steric congestion is less severe than in the DAN-P⁺R₃ salts. In the cation **12b**, $d(\text{N...P}) = 2.88, 2.78, 2.78 \text{ \AA}$ [47] is between $d(\text{N...P})$ in **12a** and $d(\text{N...P})$ in **5c-f** which is along the lines of our interpretation.

After all, we feel safe to conclude that the geometry of all these compounds is governed by the steric situation and that N→P dative bonding nowhere plays a detectable role.

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Experimental Section

Syntheses

Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany. The assignments of the ¹³C NMR signals are in part tentative.

(8-Dimethylamino-naphth-1-yl)(methyl)(phenyl)phosphine (**5**, R = Me, P = P(Me)Ph). All operations were carried out under argon. From 17.0 ml (103 mmol) of 1-dimethylamino-naphthalene, dissolved in 40 ml of anhydrous diethylether, and 60.0 ml (96.0 mmol) of a commercial 1.6 M solution of butyl lithium in *n*-hexane, a suspension of crystalline 8-dimethylamino-naphth-1-yl lithium was prepared, as previously described [1]. At -67 to -60 °C, 12.25 ml (90.3 mmol) commercial dichloro(phenyl)phosphine was added within 5 min. The stirred mixture was then allowed to warm up to -35 °C within 2 h and then to +3 °C within 10 min. After *ca.* 15 h at 0 °C, a Grignard solution prepared from 7.0 ml (112 mmol) of iodomethane in 20 ml of anhydrous diethylether and 3.0 g (123 mg-atom) of magnesium turnings was added within 40 min so that the temperature of the mixture did not exceed +20 °C. The mixture was stirred for 18 h and then hydrolyzed by addition of 1 ml of ethanol and 2.7 ml of water. The yellow solution was removed with a syringe, the residue stirred with 30 ml of diethylether and this ethereal extract added to the previously separated liquid. After evaporation of the solvents, 12.75 g of a slowly crystallizing, yellow oil were obtained which, according to ¹H NMR analysis consisted of 92% phosphine and 8%

1-dimethylamino-naphthalene. – ^1H NMR (200 MHz, in CDCl_3): δ 1.48, d, $^2J(\text{HP}) = 6.9$ Hz, 3 H (P- CH_3); 2.09, s, 3 H (N- CH_3^{A}); 2.61, s, 3 H (N- CH_3^{B}); 7.11 - 7.84, m, 11 H (Ar-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, in CDCl_3): δ 16.83, d, $^1J(\text{CP}) = 17.0$ Hz (P- CH_3); 44.60, d, $^5J(\text{CP}) = 3.1$ Hz; 47.65, d, $^5J(\text{CP}) = 12.3$ Hz (N($\text{CH}_3^{\text{A,B}}$))₂; 20 signals between 118.54 and 144.59 ppm; 151.9, d, $^3J(\text{CP}) = 3.2$ Hz (C(8) of DAN). – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, in CDCl_3): δ -19.08. – MS (pos. CI / isobutane): $m/z = 295$ (M+2, 20%), 294 (M+1, 100%), 293 (M, 44%), 278 (M-Me, 23%).

(8-Dimethylamino-naphth-1-yl)di(methyl)(phenyl)-phosphonium iodide (**5c**, anion: I^-). From a solution of 1.20 g (ca. 3.8 mmol) of crude (DAN)(methyl)(phenyl)-phosphine and 0.81 ml (13.0 mmol) of iodomethane in 3.5 ml of toluene, the title compound separated within 30 min. After addition of 5 ml of toluene and 40 ml of diethylether, 1.60 g (97%) of product was collected; m.p. 231 - 245 °C. From a solution in 80 ml of dichloromethane to which 40 ml of cyclohexane was added, 1.39 g (84%) crystallized during slow evaporation of the dichloromethane within 10 days; m.p. 238-241 °C. – ^1H NMR (200 MHz, CD_2Cl_2): δ 2.01, s, 6 H (N(CH_3)₂); 2.57, d, $^2J(\text{HP}) = 12.3$ Hz, 6 H (P⁺(CH_3)₂); 7.44 - 8.55, m (11 Ar-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, in CDCl_3): δ 15.79, d, $^1J(\text{CP}) = 61.3$ Hz (P⁺(CH_3)₂); 47.34, s (N(CH_3)₂); 113.53, d, $^1J(\text{CP}) = 95.2$ Hz (Ph-C(ipso)); 121.63, s (C(7)); 125.48, d, $^1J(\text{CP}) = 98.7$ Hz (C(1)); 126.35, d, $^3J(\text{CP}) = 15.8$ Hz (C(3)); 127.56, s (C(6)); 128.65, s (C(5)); 129.32, d, $^2J(\text{CP}) = 11.1$ Hz (Ph-C(ortho)); 130.14, d, $^3J(\text{CP}) = 13.5$ Hz (Ph-C(meta)); 130.45, d, $^3J(\text{CP}) = 5.3$ Hz (C(10)); 133.28, d, $^4J(\text{CP}) = 3.1$ (C(4)); 135.95, d, $^2J(\text{CP}) = 8.9$ Hz (C(9)); 136.64, d, $^4J(\text{CP}) = 3.6$ Hz (Ph-C(para)); 139.09, d, $^2J(\text{CP}) = 11.8$ Hz (C(2)); 150.20, s (C(8)). – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, in CDCl_3): δ +20.13.

(8-Dimethylamino-naphth-1-yl)di(methyl)(phenyl)-phosphonium tetraphenylborate (**5c**). A solution of 467 mg (1.07 mmol) of the corresponding iodide (see before) in 30 ml of methanol was added to a solution of 390 mg (1.14 mmol) of sodium tetraphenylborate in 10 ml of methanol. **5c** precipitated immediately. After addition of 10 ml of water, it was filtered off; yield 651 mg (97%), m.p. 156 - 157.5 °C. For the X-ray structure determination and the elemental analysis, a sample was recrystallized from acetone / water (3:2); m.p. 156.5 - 157 °C. – ^1H NMR (300 MHz, in CD_2Cl_2): δ 1.79, d, $^2J(\text{HP}) = 12.0$ Hz, 6 H (P⁺(CH_3)₂); 1.91, s, 6 H (N(CH_3)₂); 6.80 - 8.34, m, 31 H (Ar-H). – $\text{C}_{44}\text{H}_{43}\text{BNP}$ (627.6): calcd. N 2.23, P 4.93; found N 2.28, P 4.95.

(8-Dimethylamino-naphth-1-yl)(ethyl)(methyl)(phenyl)phosphonium iodide (**5d**, anion: I^-). Crystals of the corresponding bromide separated from a solution of

1.20 g (ca. 3.8 mmol) of crude (DAN)(methyl)(phenyl)-phosphine and 1.50 ml (20.1 mmol) of bromoethane in 3.5 ml of toluene. After 33 d, the mixture was poured into 40 ml of diethylether and the bromide filtered off. It liquified on the funnel and was dissolved in dichloromethane. After evaporation of the latter, the bromide was dissolved in 15 ml of water. Upon addition of 3.56 g of potassium iodide in 10 ml of water, the phosphonium iodide precipitated as an oil. 946 mg (56%) of non-crystalline material was isolated by extraction of the mixture with dichloromethane and evaporation. Upon slow evaporation of a solution in dichloromethane / cyclohexane (3:1), 770 mg (45%) of slightly yellow crystals was obtained; m.p. 208 - 211 °C. – ^1H NMR (200 MHz, in CD_2Cl_2): δ 1.09, dt, $^3J(\text{HP}) = 19.4$ Hz, $^3J(\text{HH}) = 7.5$ Hz, 3 H (P⁺ CH_2CH_3); 1.87, br s, and 2.09, br s, 3+3 H (N(CH_3)₂^{A,B}); 2.51, d, $^2J(\text{HP}) = 12.0$ Hz, 3 H (P⁺ CH_3); 2.89, ddq, $^2J(\text{HP}) = 13.1$ Hz, $^2J(\text{HH}) = 15.0$ Hz, $^3J(\text{HH}) = 7.5$ Hz, 1 H, and 3.11, ddq, $^2J(\text{HP}) = 11.0$ Hz, $^2J(\text{HH}) = 15.0$ Hz, $^3J(\text{HH}) = 7.5$ Hz, 1 H (P⁺ $\text{CH}^{\text{A}}\text{H}^{\text{B}}$), 7.42 - 8.34, m, 10 H (Ar-H); 8.51, ddd, $^3J(\text{HP}) = 17.2$ Hz, $^3J(\text{HH}) = 7.4$ Hz, $^4J(\text{HH}) = 1.2$ Hz, 1 H (C(2)-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, in CD_2Cl_2): δ 7.17, d, $^2J(\text{CP}) = 14.4$ Hz (P⁺ CH_2CH_3); 11.99, d, $^1J(\text{CP}) = 61.1$ Hz (P⁺ CH_3); 21.30, d, $^1J(\text{CP}) = 55.9$ Hz (P⁺ CH_2CH_3); 111.38, d, $^1J(\text{CP}) = 91.7$ Hz (Ph-C (ipso)); 121.39, s (C(7)); 123.88, d, $^1J(\text{CP}) = 96.6$ Hz (C(1)); 126.12, s (C(7)); $^3J(\text{CP}) = 15.3$ Hz (C(3)); 127.34, s (C(6)); 128.47, s (C(5)); 129.52, d, $^2J(\text{CP}) = 10.4$ Hz (Ph-C (ortho)); 129.93, d, $^3J(\text{CP}) = 13.2$ Hz (Ph-C (meta)); 130.48, d, $^3J(\text{CP}) = 4.5$ Hz (C(10)); 133.15, d, $^4J(\text{CP}) = 3.1$ Hz (C(4)); 135.92, d, $^2J(\text{CP}) = 10.4$ Hz (C(9)); 136.45, d, $^4J(\text{CP}) = 3.6$ Hz (Ph-C (para)); 139.15, d, $^2J(\text{CP}) = 10.7$ Hz (C(2)); 150.18, d, $^3J(\text{CP}) = 2.4$ Hz (C(8)). – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, in CD_2Cl_2): δ +26.74 Hz.

(8-Dimethylamino-naphth-1-yl)(ethyl)(methyl)(phenyl)phosphonium tetraphenylborate (**5d**). Upon addition of a solution of 244 mg (0.54 mmol) of the corresponding phosphonium iodide in 15 ml of methanol to a solution of 246 mg (0.72 mmol) of sodium tetraphenylborate in 10 ml of methanol, a precipitate formed which dissolved upon addition of 25 ml of ethanol and heating. **5d** crystallized after addition of 10 ml of water to the hot solution; yield 331 mg (95%); m.p. 174-176.5 °C. For the X-ray structure determination and the elemental analysis, **5c** was recrystallized from acetone / water (ca. 3:1); m.p. 175 - 176 °C. – ^1H NMR (200 MHz, in CD_2Cl_2): δ 0.89, dt, $^3J(\text{HP}) = 18.5$ Hz, $^3J(\text{HH}) = 7.5$ Hz, 3H, (P⁺ CH_2CH_3); 1.77, br s, and 2.03, br s, 3+3 H (N($\text{CH}_3^{\text{A,B}}$))₂; 1.84, d, $^2J(\text{HP}) = 11.8$ Hz, 3 H (P⁺ CH_3); 2.28, dd, $^2J(\text{HP}) = 9.6$ Hz, $^3J(\text{HH}) = 7.5$ Hz, 2 H (P⁺ CH_2); 6.78 - 8.32, m, 31 H (Ar-H). – $\text{C}_{45}\text{H}_{45}\text{BNP}$ (641.6): calcd. N 2.18, P 4.83; found N 2.27, P 4.86.

1-Isopropylamino-naphthalene. Upon heating 100 g (0.70 mol) of 1-amino-naphthalene and 80 ml (0.80 mol) of 2-iodo-propane, a vigorous reaction set in which was moderated by cooling and ceased after *ca.* 10 min. The mixture was heated with 25 ml cyclohexane. After decantation of the liquid, 50 g of sodium hydroxide, 650 ml of water, 200 ml 2N potassium hydroxide, 50 ml of ethanol and 300 ml of dichloromethane were added. Evaporation of the organic phase yielded 129 g of crude product from which 110 g (85%) of almost colourless material was obtained by fractional distillation; b. p. 160 - 162 °C/11 torr, $n_D^{20} = 1.6288$. – ^1H NMR (90 MHz, in CDCl_3): δ 1.25, d, $^3J(\text{HH}) = 6.3$ Hz, 6 H ($\text{NCH}(\text{CH}_3)_2$); 3.73, sept, $^3J(\text{HH}) = 6.3$ Hz, 1 H (NCH); 4.08, br s, 1 H (NH); 6.49 - 7.88, m, 7H.

1-[(Isopropyl)(methyl)amino]naphthalene. 92.7 g (0.50 mol) 1-isopropylamino-naphthalene and 60.0 ml (0.63 mol) of dimethylsulfate reacted exothermally. After 90 min and addition of 40 ml of toluene, the mixture was heated to 130 °C (bath temperature) for 90 min. After cooling, 100 ml of 30% aqueous sodium hydroxide, 20 ml of ethanol and 20 ml of conc. aqueous ammonia were added. A vigorous reaction occurred. When it had subsided, the mixture was heated to *ca.* 80 °C for 40 min. After cooling, 600 ml of water was added. The mixture was extracted twice with 120 ml of *n*-hexane. The combined organic phases were concentrated to *ca.* 150 ml and briefly heated with 40 ml of acetic anhydride, cooled and treated with 30 g of sodium hydroxide dissolved in 200 ml of water. After the exothermic reaction had subsided, the organic material was extracted into 300 ml of *n*-hexane, recovered by evaporation and finally distilled; yield 74.68 g of a slightly yellow oil, b. p. 139 - 141 °C/11 torr. Chromatography on silica gel in *n*-pentane yielded 41.15 g (41%) of the title compound as an oil. – ^1H NMR (90 MHz, in CDCl_3): δ 1.12, d, $^3J(\text{HH}) = 6.8$ Hz, 6 H ($\text{NCH}(\text{CH}_3)_2$); 2.73, s, 3 H (NCH_3); 3.59, sept, $^3J(\text{HH}) = 6.8$ Hz, 1 H (NCHMe_2); 6.99 - 8.30, m, 7 H (*Ar-H*).

[8-(Isopropyl)(methyl)amino-naphth-1-yl]di(phenyl)phosphine (5, R = CHMe₂, P = PPh₂). The reaction was performed in an argon atmosphere. 20.0 ml (32.0 mmol) of a commercial 1.6 M solution of *n*-butyl lithium in *n*-hexane was added to a solution of 6.30 g (31.6 mmol) of 1-(isopropyl)(methyl)amino-naphthalene in 8 ml of anhydrous diethylether. During 39 d at *ca.* 25 - 30 °C, a yellow product crystallized. After 10 more days, the red liquid was removed with a syringe, the crystals washed with 5 ml of anhydrous diethylether and suspended in 10 ml of diethylether. 1.80 ml (10.0 mmol) of chlorodiphenylphosphine was added and the mixture kept at room temperature for 20 h. Conventional workup yielded 3.21 g crude phosphine, 2.24 g (58%) after recrystallization from acetone/water (10:1), yellow crystals, m. p.

138 - 141 °C. Repeated recrystallization from acetone / water and methanol / water raised the m. p. to 150 - 151 °C. – ^1H NMR (300 MHz, in CDCl_3): δ 0.93, d, $^3J(\text{HH}) = 6.4$ Hz, 3 H, and 1.16, d, $^3J(\text{HH}) = 6.6$ Hz, 3+3 H ($\text{NCH}[\text{CH}_3^{\text{A,B}}]_2$); 1.99, s, 3 H (NCH_3); 3.28, sept, $^3J(\text{HH}) = 6.5$ Hz, 1 H (NCHMe_2); 6.90 - 7.79, m, 16 H (*Ar-H*). – $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, in CDCl_3): δ 17.26, s, and 20.57, d, $^6J(\text{CP}) = 9.7$ Hz ($\text{NCH}[\text{CH}_3^{\text{A,B}}]_2$); 38.04, d, $^5J(\text{CP}) = 1.8$ Hz (NCHMe_2); 55.84, d, $^5J(\text{CP}) = 6.0$ Hz (NCH_3); 24 signals from 122.21 to 150.74. – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, in CDCl_3): δ -2.10. – MS (pos. CI/isobutane): *m/z* = 386 (M+3, 8%), 385 (M+2, 27%), 384 (M+1, 100%), 383 (M, 64%). – $\text{C}_{26}\text{H}_{26}\text{NP}$ (383.5): calcd. N 3.65, P 8.08; found N 3.78, P 7.94.

[8-(Isopropyl)(methyl)amino-naphth-1-yl](methyl)di(phenyl)phosphonium iodide (5e, anion: I⁻) crystallized from a solution of 530 mg (1.38 mmol) of [8-(isopropyl)(methyl)amino-naphth-1-yl]di(phenyl)phosphine and 1.00 ml (16.1 mmol) of iodomethane in 14 ml of toluene; yield 699 mg (96%), m. p. 268 - 270 °C, 273 - 275 °C after recrystallization from ethyl acetate / toluene (3:2). – ^1H NMR (300 MHz, in CD_2Cl_2): δ 0.42, d, $^3J(\text{HH}) = 6.4$ Hz, and 0.45, d, $^3J(\text{HH}) = 6.3$ Hz, 3+3 H ($\text{NCH}(\text{CH}_3^{\text{A,B}})_2$); 2.10, s, 3 H (NCH_3); 2.93, sept, $^3J = 6.5$ Hz, 1 H (NCHMe_2); 3.16, d, $^2J(\text{HP}) = 13.3$ Hz, 3 H (P^+CH_3); 7.12 - 8.26, m, 16 H (*Ar-H*). – $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, in CDCl_3): δ 14.16, d, $^1J(\text{CP}) = 64.2$ Hz (P^+CH_3); 17.04, s, and 19.93, s ($\text{NCH}[\text{CH}_3^{\text{A,B}}]_2$); 38.74, s (NCH_3); 57.31, s (NCHMe_2); 113.22, d, $^1J(\text{CP}) = 93.2$ Hz, 123.58, d, $^1J = 93.5$ Hz and 124.27, d, $^1J(\text{CP}) = 87.0$ Hz ((C(1), Ph-C (ipso)^{A,B}); 125.19, d, $^3J(\text{CP}) = 16.0$ Hz (C(3)); 125.35, s (C(7)); 127.53, d, $^4J(\text{CP}) = 1.0$ Hz (C(5)); 127.63, s (C(6)); 130.13, d, $^3J = 12.7$, and 130.41, d, $^2J(\text{CP}) = 12.3$ Hz (Ph-C(ortho)^{A,B}); 131.67, d, $^2J(\text{CP}) = 9.9$ Hz, and 132.62, d, $^3J(\text{CP}) = 9.4$ (Ph-C(meta)^{A,B}); 133.18, d, $^3J = 5.0$ Hz (C(10)); 133.86, d, $^4J = 2.9$ Hz, and 134.09, d, $^4J(\text{CP}) = 2.6$ Hz (Ph-C(para)^{A,B}); 135.05, d, $^2J(\text{CP}) = 9.0$ Hz (C(9)); 136.50, d, $^4J(\text{CP}) = 3.7$ Hz (C(4)); 141.39, d, $^2J(\text{CP}) = 12.9$ Hz (C(2)); 146.39, d, $^3J = 2.2$ Hz (C(8)). – $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CDCl_3): δ +24.84.

[8-(Isopropyl)(methyl)amino-naphth-1-yl](methyl)di(phenyl)phosphonium tetraphenylborate (5e) precipitated from a solution of 315 mg (0.60 mmol) of the corresponding iodide in 20 ml of methanol upon addition of a solution of 252 mg (0.74 mmol) of sodium tetraphenylborate in 10 ml of methanol. 30 ml of water was added to complete the precipitation; yield 405 mg (94%), m. p. 205 - 208 °C. For the X-ray structure determination and the elemental analysis, a sample was recrystallized from ethyl acetate / acetone (3:1); m. p. 208 - 210 °C. – ^1H NMR (200 MHz, in CD_2Cl_2): δ 0.38, d, $^3J(\text{HH}) = 6.5$ Hz, and 0.39, d, $^3J(\text{HH}) = 6.4$ Hz, 3+3 H ($\text{NCH}(\text{CH}_3^{\text{A,B}})_2$); 2.07, s 3 H

(NCH₃); 2.66, d, ²J(HP) = 13.3 Hz, 3 H (P⁺CH₃); 2.82, sept, ³J(HH) = 6.5 Hz, 1 H (NCHMe₂); 6.79-8.24, m, 36 H (Ar-H). – C₅₁H₄₉BNP (717.7): calcd. N 1.95, P 4.31; found N 2.17, P 4.39.

(8-Dimethylamino-naphth-1-yl)(ethyl)di(phenyl)-phosphonium tetrphenylborate (**5f**). The synthesis has been described in [7].

1-Bromo-8-dibenzylamino-naphthalene (DBAN-Br). A mixture of 11.18 g (50.3 mmol) of 1-amino-8-bromonaphthalene (m. p. 87 - 88.5 °C) [48], 18.0 ml (151 mmol) of benzyl bromide, 12.36 g (89 mmol) of potassium carbonate and 80 ml of diglyme was refluxed 3 h in an atmosphere of argon, then cooled down to *ca.* 100 °C, diluted with 100 ml of water, kept at *ca.* 100 °C for 30 min and at RT for *ca.* 15 h. 250 ml of toluene was added, the organic layer washed with water and filtered through a multi-layer column consisting of sodium sulfate, silica gel, sodium sulfate, basic aluminium oxide and again sodium sulfate. Evaporation of the toluene yielded 23.8 g of a reddish brown oil. This was dissolved in 300 ml of hot ethanol and the solution boiled with charcoal. After cooling, the title compound crystallized slowly; yield 11.88 g of bright yellow crystals, m. p. 106 - 108 °C. A second crop (2.98 g, m. p. 104 - 107 °C) crystallized from the filtrate after addition of 30 ml of water; total yield 73%. For the X-ray structure determination and the elemental analysis, a sample was recrystallized first from cyclohexane / *n*-pentane (1:1) and then from ethanol; yellow needles, m. p. 109-111 °C. – ¹H NMR (200 MHz, in CDCl₃): δ 4.19, d, ²J(HH) = 14.3 Hz, 2 H (N(CH^AH^BPh)₂); 4.29, d, ²J(HH) = 14.2 Hz (N(H^AH^BPh)₂); 6.74-7.88, m, 16 H. – ¹³C NMR (50.3 MHz), in CDCl₃): δ 57.88, t (N(CH₂Ph)₂); 118.13, s; 120.50, d; 123.56, d; 125.61, d; 125.74, d; 126.35, s; 126.96, d; 127.88, d; 129.03, d, 133.33, d, 136.75, s; 137.61, s; 146.68, s. – MS (EI, 70 eV): *m/z* = 404 (¹³C⁸¹Br-M, 15%), 403 (⁸¹Br-M, 57%), 402 (¹³C/⁷⁹Br-M, 17%), 401 (⁷⁹Br-M, 54%), 322 (16%), 312 (⁸¹Br-M – C₇H₇, 29%), 310 (⁷⁹Br-M – C₇H₇), 230 (79%), 91 (C₇H₇, 100%). – C₂₄H₂₀BrN (402.3): calcd. Br 19.86, N 3.48; found Br 19.8, N 3.55.

X-ray diffraction

All measurements of diffractive data were performed on a Kuma KM4CCD *κ*-axis diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were positioned at 65 mm from the KM4CCD camera. 612 (for **5c** and **5e**) and 2120 (for the other crystals) frames were measured at 0.6 - 0.8° intervals with a counting time of 6 - 45 sec. The data were corrected for Lorentz and polarization effects. No absorption correction was applied with exception of **5e**. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw, Poland) suite of programs.

The structures were solved by direct methods [49] and refined using SHELXL [50]. The refinement was based on *F*² for all reflections except those with negative *F*². Weighted *R* factors *wR* and all goodness-of-fit *S* values are based on *F*². Conventional *R* factors are based on *F* with *F* set to zero for negative *F*². The *F*_o² > 2s(*F*_o²) criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on *F*² are about twice as large as those based on *F*. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. [51].

Crystal data

5c: C₄₄H₄₃B₁N₁P₁, *M* = 627.57, colourless, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 14.659(3), *b* = 9.0464(18), *c* = 26.558(5) Å, β = 92.27(3)°, *V* = 3519.1(12) Å³, *D*_c = 1.185 mg/mm³, μ = 0.110 mm⁻¹, *F*(000) = 1336. A total of 66418 reflections, 8694 unique [*R*_{int} = 0.0465] at 295.0 K, final *wR*₂ = 0.1072, *R*₁ = 0.0436 (reflections with *I* > 2σ(*I*)) and goodness-of-fit = 0.806 for 597 refined parameters.

5d: C₄₅H₄₅B₁N₁P₁, *M* = 641.60, colourless, monoclinic, *P*2₁/*n*, *Z* = 4, *a* = 13.105(3), *b* = 18.045(4), *c* = 15.245(3) Å, β = 96.73(3)°, *V* = 3580.2(12) Å³, *D*_c = 1.190 mg/mm³, μ = 0.110 mm⁻¹, *F*(000) = 1368. A total of 24037 reflections, 8670 unique [*R*_{int} = 0.0428] at 295.0 K, final *wR*₂ = 0.0962, *R*₁ = 0.0442 (reflections with *I* > 2σ(*I*)) and goodness-of-fit = 0.835 for 614 refined parameters.

5e: C₅₁H₄₉B₁N₁P₁, *M* = 717.69, colourless, monoclinic, *P*2₁/*n*, *Z* = 4, *a* = 11.818(2), *b* = 19.966(4), *c* = 17.205(3) Å, β = 94.87(3)°, *V* = 4045.0(14) Å³, *D*_c = 1.178 mg/mm³, μ = 0.104 mm⁻¹, *F*(000) = 1528. A total of 80088 reflections, 10410 unique reflections, analytical absorption correction applied, [*R*_{int} = 0.055] at 295.0 K, final *wR*₂ = 0.1932, *R*₁ = 0.0682 (reflections with *I* > 2σ(*I*)) and goodness-of-fit = 1.010 for 684 refined parameters.

5f: C₅₀H₄₇B₁N₁P₁, *M* = 703.66, colourless, triclinic, *P*1̄, *Z* = 4, *a* = 12.040(2), *b* = 15.020(3), *c* = 23.210(5) Å, α = 98.46(3), β = 98.36(3)°, γ = 104.10(3), *V* = 3954(1) Å³, *D*_c = 1.182 mg/mm³, μ = 0.105 mm⁻¹, *F*(000) = 1496. A total of 38052 reflections, 7371 unique [*R*_{int} = 0.1177] at 295.0 K, final *wR*₂ = 0.1225, *R*₁ = 0.1119 (reflections with *I* > 2σ(*I*)) and goodness-of-fit = 1.278 for 994 refined parameters.

DBAN-Br: C₂₄H₂₀Br₁N₁, *M* = 402.32, yellow crystal, orthorhombic, *Pca*2₁, *Z* = 4, *a* = 15.136(3), *b* = 13.033(3), *c* = 9.4559(19) Å, *V* = 1865.4(6) Å³, *D*_c = 1.433 mg/mm³, μ = 2.210 mm⁻¹, *F*(000) = 824. A total of 11865 reflections, 3127 unique [*R*_{int} = 0.0949] at 295.0 K, final *wR*₂ =

0.1248, $R_1 = 0.0517$ (reflections with $I > 2\sigma(I)$) and goodness-of-fit = 1.053 for 316 refined parameters.

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 150873, CCDC 150874, CCDC 150875, CCDC 150876 and CCDC 150877 for **5c**, **5d**, **5e**, **5f** and **DBAN-Br**, respectively. Copies of the data can be obtained free of charge on

application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial support by the Volkswagen Foundation (Hannover) (project Experimental and theoretical conformational analysis of organic compounds in solution) is gratefully acknowledged.

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- [32] Molecule A of two independent molecules in the unit cell [11]; splay angle calculated from the atomic coordinates [11]; molecule B: $d(\text{N}\dots\text{P}) = 2.729 \text{ \AA}$.
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- Br⁻] are pseudopentacoordinated or pentacoordinated in solution... in agreement with the solid-state structures”.
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