peri-Interactions in Naphthalenes, 5 [1].

On the Impact of peri-Stress and Trityl-Stress upon the Length of N+–C Bonds in 1-Azonia-acenaphthene Cations

Gerald Dyker⁷, Marcel Hagel⁶, Gerald Henkel⁶, Martin Köckerling⁶, Christian Näther⁶, Sönke Petersen⁴, and Günter Paulus Schiemenz⁴

a Fakultät für Chemie der Ruhr-Universität, D-44780 Bochum, Germany
b Institut für Synthesechemie der Universität Duisburg, D-47048 Duisburg, Germany
c Institut für Anorganische Chemie der Universität, D-24098 Kiel, Germany
d Institut für Organische Chemie der Universität, D-24098 Kiel, Germany

Reprint requests to Prof. Dr. G. P. Schiemenz. Fax: +49 (0)431 880 1558.

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peri-Naphthalenes, Steric Effects

In the 1-azonia-acenaphthene salts 6b and 9, the N+-Cpery bond is modestly elongated. While no clear-cut influence of the peri-stress is obvious, incorporation of Cpery in a triarylmethyl structure has a bond-lengthening effect. However, the stretching forces are insufficient to restore the ideal geometry of the naphthalene skeleton.

Introduction

The pentacovalent phosphorus atoms of bis(o-phenylenedioxy)phosphoranes are sufficiently electrophilic to react with the nucleophilic nitrogen atoms of tertiary amines to give zwitterionic species with hexacovalent phosphorus and a new “dative bond” [2] whose symbol, N→P, coined in analogy of the traditional representation of amine oxides, R₃N—O [3], is equivalent to the more appropriate symbol N⁺→P⁻ (as R₃N⁺—O⁻ is for the amine oxides) [4, 5]. In [2-(dimethylamino-methyl)phenyl]bis(o-phenylenedioxy)phosphoranes (1) an almost unstrained five-membered ring is formed (1 → 3) in which the “dative N→P bond” has lengths of 200.7 to 206.3 pm [6].

In (8-dimethylamino-naphth-1-yl)bis(o-phenylenedioxy)phosphorane, DAN-P(O₂C₆H₄)₂ (2), the size of the peri-substituents would not permit the naphthalene skeleton to maintain its “natural” geometry (i.e. 120° angles throughout) which would place the nitrogen and the phosphorus atoms at a distance of 250 pm [1, 7, 8]. From d(N...N) = 279.2 pm in 1,8-bis(dimethylamino)naphthalene [9] and d(P...P) = 292.7 pm [10] - 307.0 pm [11] in 1,8-bis(diorganophosphino)naphthalenes, d(N...P)(2) = ca. 286 - 293 pm would be estimated by linear inter-

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the peri-stress. $d(\text{H}_2\text{C}-\text{CH}_2) = 154$ pm in acenaphthene [21] is not a single picometer longer than the C-C bond in ethane [22]. The double bond in acenaphthylene is 139.5 pm long [23], in a 9,10-dihydro-anthracene-9,10-diyl derivative even shorter ($d(\text{C}=\text{C}) = 135.8$ pm [24]) and thus of the same length as in ethylene ($d(\text{H}_2\text{C}=\text{CH}_2) = 135.3$ pm [25]). In a ferrocenyl derivative of 1,2-bis(methylene)acenaphthene, the peri-C-C bond ($d(\text{C}-\text{C}) = 150.9$ pm [26]) is 3 pm longer than the central C-C bond in a 1,4-diaryl-2,3-diphenyl-butaadiene ($d(\text{C}=\text{C}) = 148.0$ pm [27]) though still shorter than a C-C single bond by about the same amount. $d(\text{OC}-\text{CO}) = 153$ pm in acenaphthenquinone [28] is identical with $d(\text{OC}-\text{CO}) = 152.9$ pm (100 K) in benzil [29].

It was of interest to study in more detail to what extent such peri bonds can be stretched by peri-stress and related causes. We first turned to $\text{N}^+\text{-C}_{\text{peri}}$ bonds which, in analogy to the N-P bond in 4, can be regarded as dative bonds [2] (cf. formulae 6', 9').

(Benzyl)di(methyl)(phenyl)ammonium tetraphenyloborate (5a) serves as a model compound in which the $\text{N}^+\text{-CH}_2$ bond is free of stress. 6a was obtained when in 2-DAN-butan-2-ol (7a) the HO group was exchanged by Br (7a $\rightarrow$ 7b). In the corresponding bromide 7b, substitution of the bromine would tend to proceed by an $\text{S}_2\text{N}_1$ mechanism so that the cation 8 is a reasonable intermediate in the formation of 6a. It is, therefore, not only conceptionally but even chemically justified to call the peri-N-C bond in 6 a dative bond [2b] (cf. formula 6'). As the peribound carbon atom in 9 is part of a triaryl methyl unit and trityl salts with non-nucleophilic anions are stable, even commercially available compounds, this holds even more for 9 containing the suberenyl group (cf. formula 9'). In fact, the N-protonated bis-cation 10 is formed as its bis(tetrafluoroborate) by treatment of the tertiary alcohol 11 with tetrafluoroboric acid. Upon N-deprotonation, 10 cyclizes to give 9. $\text{N}^+\text{-C}_{\text{Ar}}$ bonds can be inferred to be weak and of "dative" character from the chemistry of di(methyl)(trityl)amine: When heated with methyl iodide in ethanol, tetra(methyl)ammonium iodide and (ethyl)(trityl) ether are obtained [30]. The facile reaction has been rationalized as starting with an N-quaternization followed by what may be called a dissociation of a dative bond [2b], capture of Ph$_3\text{C}^+$.
by ethanol and quaternization of Me$_3$N by excess Mel [30]:

$$\text{Me}_3\text{N}^\text{=}-\text{CPh}_3 + \text{Me}^+\text{I}^- \quad (= \text{"Me}_3\text{N}^\text{=}-\text{CPh}_3 1^\text{°})$$

$$\text{Me}_3\text{N} + \text{CPh}_3 1^\text{°} + \text{Me}^-\text{I} + \text{HOEt}$$

$$\text{Me}_3\text{N}^\text{=} + \text{EtO-CPh}_3^- (+ \text{HI})$$

The ready dissociation of 5b into di(methyl)-aniline and (presumably) benzyl iodide (followed by N-methylation of the amine if carried out in the presence of methyl iodide) [31] justifies to regard even the N+-CH$_3$ bonds in 5a,b as dative bonds [2b]. 6b and 9 are thus suitable models for the DAN-silanes and DAN-phosphorus compounds for which a weak dative interaction N—Si/P has been claimed [6, 13, 14, 16, 32] and in a favourable case a dative N—> P bond has been found [1].

Results and Discussion

In 5a, 6b and 9, the N+-CH$_3$ bond lengths are virtually identical (5a: 150.2 / 150.6 pm; 6b: 149.6 / 151.5 pm; 9: 149.6 / 150.8 pm). d(N-C$_\text{arom}$) is slightly, though not really significantly shorter in 6b, 9 than in 5a, d(C$_\text{peri}$-C$_\text{arom}$) in 6b, 9 to about the same degree longer than d(H$_2$C-C$_\text{Ph}$) in 5a. On the other hand, the N+-C(benzyl/peri) bond (which in 5a is ca. 4 pm longer than the N+-CH$_3$ bonds) is elongated by 5.2 pm (3.4%) in 6b and by 17.2 pm (11.1%) in 9. The increase is certainly significant, but the stretching forces are far from being able to restore the ideal naphthalene geometry.

The elongation by 5.2 pm from 5a to 6b cannot simply be ascribed to the peri-stress: Phosphonium salts exhibit a pronounced chain branching effect; e.g. d(P+-CH$_3$) = 178.2 pm (in DAN-P+(Me)(Et)Ph BPh$_4^-$), mean value [19], 178.6 pm (in DAN-P+(Me)BPh$_4^-$ [19]), d(P+-CHMe$_2$) = 183.0 pm (in P+(CHMe$_2$)$_4$, mean value [34]), d(P+-CMe$_2$) = 186.7 pm (in 4-MeC$_5$H$_3$P+-C(CH$_3$COMe)Me$_2$ [35]), 187.7 pm (in Et$_3$P+-C(OH)Me$_2$ [33]), 188.0 pm (in Ph$_3$P+-C(Me$_2$)CS$_2^-$ [36]), for d(P+-C$_\text{quaternary}$) 4.8 to 5.5% longer than d(P+-CH$_3$) in DAN-P+(Ph)Me$_2$. As steric congestion may be more severe in 6b than in these phosphonium salts, the case of P+(CMe$_3$)$_4$ may be pertinent where the distance is even d(P+-C) = 192.4 pm [37]. In 6b, the peri-C atom bound to N$^+$ is likewise quaternary so that the N$^+$-C$_\text{peri}$ bond elongation could be due entirely to an analogous chain branching effect.

In the realm of phosphonium salts, the trityl cation (4-MeOC$_6$H$_4$)$_3$P+-CPh$_3$ (d(P+-CPh$_3$) = 193.1 pm [38]) exhibits an additional elongation by ca. 5 pm (almost met by d(P-C) = 192.4 pm in P+(CMe$_3$)$_4$ where the congestion around P$^+$ is exceptional [39]). If this is ascribed to the well-known bond weakening triaryl methyl effect, a similar elongation by ca. 3% may be envisaged for 6b → 9. The actual increase, 12 pm (7.5%), is more than double that large.

For two reasons, a N-C bond weakened by both a positive charge on N and a trityl type substitution at C may be less stable than a P$^+$-C$_\text{Ph}$ bond and comparable with a C(sp$^3$)-C(sp$^3$) bond in hexaarylethanes. As a rule, tertiary phosphines are stronger nucleophiles than tertiary amines; cor-
respondingly, P+-C bonds should be less amenable to heterolytic cleavage than N+-C bonds and in that sense stronger. In hexaarylethanes, part of the bond lengthening is ascribed to steric crowding [40]. Since N-C bonds are shorter than P-C bonds, this effect should be more important for N+-CAR3 than for P+-CAR3 (note that P+(CMe3)4 can be synthesized [37] and N+(CMe3)4 cannot; cf. Hüning’s base, EtN(CHMe2)2 [41]). In a 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene, the C(sp3)-C(sp3) bond was found to be 10 pm (6.7%) longer than in ethane and in acenaphthene [42]. When the four aryl groups attached to the 9,10-dihydro-phenanthrene are replaced by two naphthalene-1,8-diy1 units, i.e. the hexarylethane C-C bond exposed to a twofold peri-stress, this bond is even shorter (d(C-C) = 161.2 pm [43]). Even a threefold peri-stress and a benzo-cyclobutene stress in conjunction with a twofold peri-stress were unable to stretch the respective bond [44] though some benzo-cyclobutene-derived hexaarylethane structures with significantly longer C(sp3)-C(sp3) bonds are known [45] (d(C-C) = 171.3 pm [46], 172.0 pm [47]). It emerges that C-C bonds expand under the influence of a double trityl effect, but even then are insensitive towards the peri-stress, and that N+-CAR3 bonds behave likewise. However, d(N+-C-peri)(9) = 171.9 pm > d(C-C) = ca. 162 pm in the acenaphthene-type propellanes [43, 44] indicates that the dative bond N—C is considerably more sensitive towards the trityl effect than the peri-C-C bond. For a fair comparison, d(N-C) < d(C-C) has to be taken into account (e.g. d(C-C) in ethane 4 pm longer than d(N-CH3) in 5a, 6b, 9).

In every other respect, the structural details of 6b and 9 are un conspicuous. In 9, the three bay angles add to 336.2° so that the negative splay angle [48] is −23.8°. As is the rule for peri-disubstituted naphthalenes with intersubstituent repulsion (i.e. with positive splay angles) [1], the angle C(1)-C(9)-C(8) is the largest of the bay angles. As a consequence of the short distance d(N+-C) and the negative splay angle, d(C(1)...C(8)) = 233.8 pm is shorter than in ideal naphthalene, and d(C(4)...C(5)) = 252.5 pm is longer. A short d(N-C-peri) is best accommodated when the N-C bond is coplanar with the naphthalene plane; in fact, the C10 skeleton is almost planar, and the dihedral angle C-peri-C(1)...C(8)-N, −1.1°, is close to zero. The Me groups at N are situated almost symmetrically in positions anticlinal to the C(1)...C(8) connecting line (dihedral angles H3-C-N-C(8)...C(1) = −119.9 and +121.7°, i.e. close to 120°). The somewhat bent suberenyl system bound to C(1) is virtually perpendicular to the C10 plane. Likewise, the C-peri-bound carbon atoms are in anticlinal positions and almost symmetrically positioned above and below the C10 plane (dihedral angles C-C-peri-C(1)...C(8) = +115.5° and −113.2°).

In 6b, C-peri is a stereogenic centre. The salt crystallized as a racemate in which the Me and Et groups are disordered; refinement was performed with a split model. As a consequence of d(N-C-peri)(6b) < d(N-C-peri)(9), the bay angles are even smaller (sum 328.4°), and the negative splay angle larger
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Table 1. Selected structural data of 5a, 6b and 9 (distances d in pm, angles in degrees, esd's in parentheses; numbering of the naphthalene carbon atoms according to IUPAC rules).

<table>
<thead>
<tr>
<th></th>
<th>5a</th>
<th>6b</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(N-CH₃)</td>
<td>150.2(2)</td>
<td>149.6(2)</td>
<td>149.6(5)</td>
</tr>
<tr>
<td>d(N-C₆) [5a: d(N-CH₂)]</td>
<td>150.6(2)</td>
<td>151.5(2)</td>
<td>150.8(5)</td>
</tr>
<tr>
<td>d(C₆-C₁)</td>
<td>154.7(2)</td>
<td>159.9(3)</td>
<td>171.9(5)</td>
</tr>
<tr>
<td>d(N-C₈) [5a: d(N-C(1)₈)benzy]</td>
<td>152.0(3)</td>
<td>151.9(3)</td>
<td>152.0(6)</td>
</tr>
<tr>
<td>d(C₈-C₁)</td>
<td>149.9(2)</td>
<td>148.8(2)</td>
<td>148.2(5)</td>
</tr>
<tr>
<td>d(C₁-C₈)</td>
<td></td>
<td>231.1</td>
<td>233.8</td>
</tr>
<tr>
<td>d(C₄-C₃)</td>
<td></td>
<td>254.5</td>
<td>252.5</td>
</tr>
</tbody>
</table>

Angles

C₆-C₁-C₈ [5a: H₂C-C(1-2,6)benzy] | 119.8(2) | 112.53(18) | 112.3(3) |
C₁-C₈-C₁ | 121.1(2) |
N-C₈-C₁ [5a: N-C(1-2,6)phenyl] | 118.7(2) | 107.65(17) | 110.3(3) |
N-C₁-C₈ | 121.0(2) |

Sum | 328.42 | 336.2 |
Splay angle | 31.58 | -23.8 |

Dihedral angles

C₆-C₁-C₈-N [5a: H₃C-N(1-2,6)phenyl] | -98.5 | -119.9 |
C₆-C₁-N-C₈ | 143.6 | 121.7 |
C₆-C₁-C₈ | 138.4 | 115.5 |
C₆-C₁-N-C₈ | -93.5 | -113.2 |

(−31.6°), C₁-C₈-C₈ again being the largest bay angle. As expected, d(C₁-C₈) = 231.1 pm is even shorter than in 9, and d(C₄-C₃) = 254.5 pm is 2 pm longer. While the naphthalene skeleton is nearly planar, surprisingly the five-membered heterocycle is considerably twisted (dihedral angle N-C₈...C₁-C₆ −19.9°). Correspondingly, the N-bound Me groups as well as the C₆-bound carbon atoms are still in anticlinal, but skew positions (see Table 1).

Conclusion

The dative bond N—C in 6b is slightly longer than the corresponding bond in the open chain model compound 5a, but since the elongation may be due to a chain branching effect, there is no evidence for a stretching caused by the peri-stress of the naphthalene skeleton.

Even in peri-disubstituted naphthalenes of the hexaarylethane type, no bond stretching due to the peri-stress is discernible. On the other hand, in such molecules, the triphenylmethyl effect does expand peri-bonds, and this effect is more pronounced for the dative bond N—C in 9 than for peri-C-C bonds. However, the stretching is modest (7.5% from 6b to 9) and does not enable the naphthalene skeleton to return to its natural geometry. As the N—C bond is more amenable to stretching than the peri-C-C bond, it is possible that other bonds such as the hypercoordinate N-P bonds in 3 and 4 are even more sensitive so that a modest stretching caused by the peri-stress is conceivable [1], though other factors may have the same result [20]. On the other hand, a stretching of such bonds by about one third of its length to attain interatomic distances which strongly exceed the ideal peri distance seems impossible. To the best of present knowledge, then, d(N...Si/P) = ca. 285 ± 15 pm in DAN-silanes and DAN-phosphorus compounds are the consequence of steric repulsion rather than of weak attraction due to dative bonding.

Experimental

(Benzyl)di(methyl)(phenyl)ammonium tetraphenylborate (5a) precipitated when equimolar aqueous solutions of the corresponding bromide 5 (X = Br) [49] and sodium tetraphenylborate were united, and was recrystallized from acetone. M.p. 212 - 213 °C. – ¹H-NMR (500.13 MHz, (CD₃)₂CO): δ = 3.77 (s, 6 H, NMe₂), 5.15 (s, 2 H, CH₂), 6.76 – 7.86 (7 m, 30 H, H₃). 2-(8-Dimethylamino-naphth-1-yl)-butan-2-ol (7a): A commercial 1.6 M solution of n-butyllithium in n-hexane (81 ml) was added to 1-dimethylaminonaphthal-
ene (15 ml, 0.13 mol) in anhydrous diethyl ether (50 ml).
The mixture was kept under argon for 3 d; then butan­
t-2-one (11.5 ml, 0.13 mol) was added. After hydrolytic
workup, the crude carbinol was chromatographed on sil­
ica (cyclohexane / diethyl ether 1:1). The fraction with
precipitated from
was filtered off and dissolved in methanol.
the yield was 3.90 g (58%). M. p. 191 - 193 °C. - 1H-NMR
(200.13 MHz, CDCl3): 0.77 (t, J = 7 Hz, 3H, CH2-CH3),
1.62 (s, 3H, CH3), 1.71 (s, 3H, HO-CH3), 1.83 (dq, 2J =
13.6 Hz, 3J = 7.4 Hz, 1H, CH3CH2CH3), 1.97 (dq, 2J =
13.6 Hz, 3J = 7.5 Hz, 1H, CH3CH2CH3), 2.67 (3H, N-C6H5),
2.86 (3H, N-C6H5), 7.32 - 7.75 (m, 6H, H-arom), 10.67 (s,
1H, OH). - 13C-NMR (50.3 MHz, CDCl3): δ = 8.88 (q,
CH2-CH3), 29.70 (q, HO-CH3), 37.95 (t, CH2-CH3), 45.67 (q,
N-C6H5), 48.03 (q, N-C6H5), 75.50 (s, HO-C), 120.22 (d),
124.75 (d), 124.82 (d), 126.79 (d), 128.50 (d), 128.87 (d),
137.29 (s), 145.01 (s), 149.41 (s). - MS (EI, 70 eV): m/z (%) =
243 (21) [M]N2, 225 (28) [M - H2O], 214 (100) [M -
C6H4]. MS (Cl): m/z = 243.1622. - C16H12NO (243.1623):
calcd. C 78.79, H 8.70, N 5.76; found C 78.70, H 8.74, N 5.85.

2-Ethyl-1,1,2-tri(methyl)-1-azonia-acenaphthene
tetraphenylborate (6b): The bromide 6a precipitated from a
solution of 7a (3.01 g, 12.4 mmol) in benzene (15 ml)
and pyridine (0.5 ml) upon dropwise addition of phos­
phorus tribromide (1.2 ml, 12.8 mmol) at −10 °C. After
2 h stirring, 6a was filtered off and dissolved in methanol.

After mixing with a solution of sodium tetraphenylborate
(4.37 g, 13 mmol) in methanol (30 ml), 6b crystallized out.
After recrystallization from dichloromethane / methanol
the yield was 3.90 g (58%). M. p. 191 - 193 °C. - 1H-NMR
(200.13 MHz, CDCl3): 0.77 (t, J = 7 Hz, 3H, CH2-CH3),
1.62 (s, 3H, C-H3), 1.66 (m, 2H, CH2-CH3), 2.37 (s,
3H, N-C6H5), 2.50 (s, N-C6H5), 6.80 - 7.98 (m, 28 H, 
H-arom). - C40H40BN (545.6): calcd. C 88.06, H 7.39, N
2.57; found C 88.17, H 7.22, N 2.81.

5-(8-N,N-Dimethylamino-1-naphthyl)-5-hydroxy-5H-
dibenzo[a,d]cycloheptene (11): A commercial 1.6 M so­
lution of n-butyllithium in n-hexane (3.85 ml) was added
to 1-dimethylaminonaphthalene (1.00 g, 5.72 mmol) in
anhydrous diethyl ether (3 ml). The mixture was stirred
under argon for 5 d; then 5H-dibenzo[a,d]cyclohepten-5-
one (suberenone, 1.20 g, 5.72 mmol) in 20 ml of dry THF
was added and stirring was continued for 5 d at reflux
temperature. After hydrolytic workup, the crude carbinol
was chromatographed on silica with toluene as eluent.
The fraction with Rf = 0.25 was crystallized from diethyl
ether to give 520 mg (24%) of 11 as a colorless solid.
M. p. 182 - 184 °C, - 1H-NMR (300.13 MHz, CDCl3): δ =
2.35 (s, 6H, CH3), 6.12 (s, 2H, 10'-H/H''-H), 6.85 (dd, J =
7.3, 1.0 Hz, 2H), 6.95 - 7.00 (m, 3H), 7.09 - 7.17 (m, 3H),
7.43 (dd, J = 8.1, 1.3 Hz, 2H), 7.48 (dd, J = 8.5, 1.6 Hz,
2H), 8.25 (dd, J = 8.0, 1.0 Hz, 2H), 9.15 (s, 1H, OH). -
13C-NMR (75.5 MHz, CDCl3): δ = 47.10 (q), 79.06 (s,
C-OH), 115.92 (d), 123.75 (d), 124.18 (d), 125.02 (d),
125.47 (d), 126.04 (d), 127.22 (d), 127.50 (d), 127.55 (d), 127.59 (d), 128.77 (d), 129.27 (s), 129.95 (d), 133.22 (s), 135.64 (s), 139.79 (s), 144.45 (s), 150.94 (s). - MS (EI, 70 eV): m/z (%): = 378 (78), 377 (23) [M⁺], 331 (5), 192 (15), 191 (100), 189 (6), 184 (6), 178 (9), 171 (12), 170 (22), 168 (8), 154 (6), 127 (5). – C₂H₂BF₄N (377.5); calc. C 85.91, H 6.14, N 3.71; found C 85.66, H 6.17, N 3.62.

Spiro-5H-dibenzo[a,d]cyclohepten-5,2'-[2H]-naphtho[1,8-bc]-N,N-dimethylpyrrolidine tetrafluoroborate (9): 0.20 ml (1.47 mmol) of tetrafluoroboric acid diethyl ether-amarine and 7.08 (dd, = 8.4, 0.9 Hz, 2H, J = 8.2, 7.2 Hz, 1H, 3-H), 7.72 (dd, d = 7.8, 1.5 Hz, 2H, C-6'-H'), 7.70 (dd, = 7.9 Hz, IH, C-4' -H'), 7.90 (d, d = 7.5 Hz, IH, C-7' -H), 8.03 ("dd", J = 8.2, 7.2 Hz, IH, C-3', H), 8.09 (d, d = 8.3 Hz, IH, C-5', H), 8.22 (d, J = 8.2 Hz, IH, C-4', H). – 13C-NMR (125.8 MHz, CDCl₃): δ = 54.72 (q), 113.23 (s, C-5'), 116.67 (d, C-7), 126.94 (d, C-4'), 127.43 (d, C-2), 127.68 (d, C-5), 128.14 (s), 128.94 (d, C-3), 129.50 (d, C-3/C-7'), 130.21 (d, C-6), 131.47 (s), 131.86 (s), 131.92 (d, C-2/C-8'), 133.04 (d, C-1/C-9'), 133.44 (d, C-10/C-11'), 133.62 (d, C-4/C-6'), 136.26 (s), 138.09 (s), 144.97 (s, C-8). – MS (EI, 70 eV): m/z (%): = 362 (27), 361 (87), 360 (7) [M⁺-BF₄⁻], 346 (16), 254 (10), 205 (9), 191 (17), 169 (10), 168 (21), 74 (16), 49 (100), 48 (25), 45 (15), 44 (12). – C₂H₂BF₄N (447.3): calc. C 72.50, H 4.96, N 3.26; found C 72.40, H 5.03, N 3.13.

Crystal structure determinations: All structures were solved with direct methods using SHELXS-97. Structure refinement was performed against F³ using SHELXL-97. For compound 9 an empirical absorption correction was applied. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with isotropic displacement parameters using a riding-model. Because no heavy atom is present in the crystal structure of compound 5a the absolute structure cannot be determined. Therefore, all Friedel equivalents were merged in the refinement. In the crystal structure of compound 6b the ethyl and the methyl group are disordered in a way that one carbon atom of each group occupies the same crystallographic position. Therefore, refinement was performed using a split model and occupancies of 50:50 for these atoms.

X-ray data of all structures have been deposited at the Cambridge Crystallographic Data Centre ((5a: CCDC-168916; 6b: CCDC-168917; 9: CCDC-163505). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax. (internat.) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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[16] C. Chuit, C. Reyé, Eur. J. Inorg. Chem. 1998, 1847 (note that in Table 3, number 35 refers to a neutral species (DAN)$_2$P(H)Ph for which d(N...P) = 270 - 273 pm is given (p. 1850)).
[39] Note that in cases of strong steric congestion, even C(sp$^3$)-C(sp$^3$) bonds are elongated: d(C-CH) = 159.9 pm in C(CHMe$_3$)$_2$ (S. I. Kozhushkov, R. R. Kostikov, A. P. Molchanov, R. Boese, J. Benet-Buchholz, P. R. Schreiner, C. Rinderspacher, I. Ghiviriga, A. de Meijere, Angew. Chem. 113, 179 (2001), Angew. Chem. Int. Ed. 40, 180 (2001)).