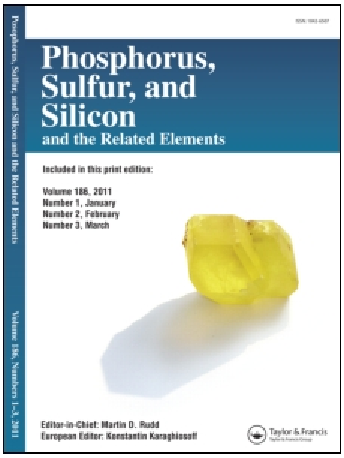

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

peri-Interactions in Naphthalenes, 15: The Concept of Incipient Bipyramidalization in 8-Dimethylaminonaphth-1-yl Silanes and Phosphonium Cations

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To cite this Article Schiemenz, Günter Paulus(2009) '*peri*-Interactions in Naphthalenes, 15: The Concept of Incipient Bipyramidalization in 8-Dimethylaminonaphth-1-yl Silanes and Phosphonium Cations', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 9, 2247 — 2262

To link to this Article: DOI: 10.1080/10426500802448013

URL: http://dx.doi.org/10.1080/10426500802448013

Phosphorus, Sulfur, and Silicon, 184:2247–2262, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802448013

peri-Interactions in Naphthalenes, 15: The Concept of Incipient Bipyramidalization in 8-Dimethylamino-naphth-1-yl Silanes and Phosphonium Cations

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The concept of a gradual transition from tetracovalent to hypercoordinated silicon and phosphorus in 8-dimethylamino-naphth-1-yl silanes and phosphonium cations is critically examined. Various procedures to quantify partial bipyramidalization fail to indicate incipient hypercoordination. In particular, deviations from tetrahedrality in trialkyl-(8-dimethylamino-naphth-1-yl) silanes and tri(alkyl/phenyl)-(8-dimethylamino-naphth-1-yl) phosphonium cations do not reflect weak N → Si/P bonding. Likewise, the distortions at the P^+ *center in tri(alkyl/phenyl)-(8-diphenylphosphino-naphth-1-yl) phosphonium cations are not indicative of dative* $P \rightarrow P^+$ *interactions.*

Keywords Deformation of bond angles; hypercoordination of phosphorus and silicon; naphthalene geometry; weak dative bonds

INTRODUCTION

Hypercoordination, i.e., the ability of an atom to engage in more than four covalent bonds, continues to intrigue chemists.[1] Sulfur, phosphorus, and silicon are capable of penta- and even hexacoordination, most easily when the ligands (or at least some of them) are strongly electronegative, as in SF_6 and PF_6^-. Such ligands are, however, not a stringent prerequisite. For example, the tetraphenylphosphonium ion reacts smoothly with phenyl lithium to yield $(C_6H_5)_5P$,[2] and even hexaarylphosphates form fairly easily.[3] Silicon is capable of forming silicate anions with five Si—C bonds in a trigonal bipyramidal (TBP) geometry

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Received 22 July 2008; accepted 1 September 2008.

The help of Dr. P. Rösner (Kiel, Germany) in preparing the artwork is gratefully acknowledged.

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not only when the two apical ligands are electronegative CF_3 groups,[4] but also with bidentate hydrocarbon ligands,[5] whose small bite angle requires less deformation in the apical/equatorial 90° coordination of a TBP than in silanes with tetrahedral silicon.

Special attention has been attracted by the interactions between the *peri*-substituents of 1,8-disubstituted naphthalenes, 1-X,8-Y-$C_{10}H_6$. In the undistorted naphthalene system (i.e., all angles 120°), the carbon atoms C(1) and C(8) have a distance of 247 pm. Since the bonds C(1)-X and C(8)-Y are parallel, this is also the ideal distance between the *peri*-substituents X and Y, if the bonds C(1)—X and C(8)—Y are of equal lengths. For X = P, Si, Y = N, the ideal *peri*-distance (PD) is 250–251 pm.[1,6–16] For $X = PR_3^+$, SiR_3, and $Y = R_2N$, formation of a bond N → P/Si has been envisaged,[17,18] but N—P/Si bonds are much shorter.[19] Because of its high electronegativity, the N atom is prone to occupy an apical position in a TBP structure[20]; though axial N—P/Si bonds in TBPs are longer than N—P/Si bonds in tetrahedral molecules,[20–22] they are still much too short to bridge the gap between N and P/Si. N → P/Si bond formation therefore necessitates a substantial deformation of the C_{10} skeleton,[9] analogous to the deformation in acenaphthene and acenaphthylene,[6,13] and the energy of the new bond would have to pay the energetic bill for such deformation. Not surprisingly, therefore, N → P/Si bonds have been found to be formed only under favorable conditions, viz. when several electronegative atoms were attached to P/Si,[1,9] whereas (8-dialkylamino-naphth-1-yl)-*triorgano* phosphonium cations and silanes exhibited the criteria of repulsion rather than attraction between N and P/Si.[1,11] This behavior has recently been found for four silanes 8-$Me_2NC_{10}H_6$-$SiMe_2R$ (**1a–d**; see Table II).[23,24] As in similar phosphonium salts (**1e**,[18] **1f–j**[11]) the splay angle between the C(1)—Si and the C(8)—N bonds is positive (+8.7, +5.3, +7.0 and +3.1°, respectively); the N $\cdots$ Si distances exceed PD = 251 pm by 54 (**1a**), 43 (**1b,c**), and 42 pm (**1d**), and the partial planarization at the nitrogen atom (as a measure of the engagement of the Me_2N group in a fourth bond[1]) is 22, 16, 15, and 21%, respectively, well within the range of strong planarization and thus indicating non-involvement in N → Si bonding. In line with these features, a twist of the naphthalene rings from planarity with Si lying above and N below the plane of the C_{10} skeleton has been interpreted as manifestation of steric repulsion between Me_2N and $SiMe_2R$.[24]

On the other hand, in a deductive rather than inductive reasoning method, "the *peri* interaction between the nitrogen and silicon substituents," expressed by formula **2a** with a N → Si bond (analogous to formula **2b** used for **1e** to express similar tenets of N/P^+ donor/acceptor

TABLE I Data of *peri*-Substituted Naphthalenes 1-$R^e_2R^aX$,8-Y-$C_{10}H_6^A$

Number (CSD-refcode)	1-$R^e_2R^aX$	8-Y	$d(X \cdots Y)$ [pm]	Splay angle	R^a	*trans*-angle R^a—$X \cdots Y$	Σ (R^e—X—R^e)	Σ (R^a—X—R^e)
1a^B (CAMGIH)	$Me_2(C_{18}H_{24}NSi)Si^C$	Me_2N	304.6	$+8^\circ\ 41'$	Me	$171^\circ\ 11'$	$340^\circ\ 22'$	$315^\circ\ 20'$
1b	$Me_2(4\text{-}O_2NC_6H_4CO\text{-}O\text{-}CH_2CH_2)Si$	Me_2N	293.8	$+5^\circ\ 32'$	Me	$173^\circ\ 17'$	$341^\circ\ 29'$	$313^\circ\ 45'$
1c	$Me_2[3,5\text{-}(O_2N)_2C_6H_3CO\text{-}O\text{-}CH_2CH_2]Si$	Me_2N	294.2	$+7^\circ\ 0'$	Me	$174^\circ\ 31'$	$342^\circ\ 35'$	$312^\circ\ 26'$
1d	Me_2R^aSi, $R^a = 2\text{-}O_2NC_6H_4CO\text{-}O\text{-}CH_2CH_2\text{-}$	Me_2N	292.7	$+3^\circ\ 4'$	R^a	$173^\circ\ 57'$	$341^\circ\ 35'$	$313^\circ\ 28'$
1e (KICDAB)	$Me_2(PhCH_2)P^+\ Br^-$	Me_2N	282.6	$+4^\circ\ 50'$	CH_2Ph	$175^\circ\ 40'$	$342^\circ\ 21'$	$313^\circ\ 2'$
1f (EDOSIZ)	$Me_2(Ph)P^+\ BPh_4^-$	Me_2N	293.9	$+5^\circ\ 52'$	Me	$175^\circ\ 36'$	$339^\circ\ 19'$	$316^\circ\ 31'$
1g (EDOSOF)	$Me(Et)(Ph)P^+\ BPh_4^-$	Me_2N	289.0	$+6^\circ\ 26'$	Et	$176^\circ\ 42'$	$340^\circ\ 43'$	$314^\circ\ 48'$
1h (EDOTAS)^E	$EtPh_2P^+\ BPh_4^-$	Me_2N	295.4	$+7^\circ\ 48'$	Ph	$176^\circ\ 40'$	$336^\circ\ 51'$	$319^\circ\ 23'$
1i (EDOTAS)^E	$EtPh_2P^+\ BPh_4^-$	Me_2N	289.2	$+7^\circ\ 22'$	Ph	$177^\circ\ 15'$	$339^\circ\ 28'$	$316^\circ\ 18'$
1j (EDOSUL)	$MePh_2P^+\ BPh_4^-$	$Me(i\text{Pr})N$	295.9	$+6^\circ\ 68'$	Ph	$176^\circ\ 52'$	$340^\circ\ 32'$	$315^\circ\ 0'$
3a (DECYOZ)	Me_3Si	Me_3Si	380.3	$+16^\circ\ 26'$	Me	$173^\circ\ 41'$	$337^\circ\ 58'$	$318^\circ\ 14'$
3b (DECYOZ)	Me_3Si	Me_3Si	380.3	$+16^\circ\ 26'$	Me	$172^\circ\ 52'$	$339^\circ\ 58'$	$315^\circ\ 41'$
4a (TMGNPA)	Me_3Ge	Me_3Ge	380.9	$+16^\circ\ 34'$	Me	$172^\circ\ 32'$	$340^\circ\ 4'$	$315^\circ\ 40'$
4b (TMGNPA)	Me_3Ge	Me_3Ge	380.9	$+16^\circ\ 34'$	Me	$172^\circ\ 26'$	$340^\circ\ 26'$	$315^\circ\ 10'$
5a (TMGNPB)	Me_3Sn	Me_3Sn	386.4	$+16^\circ\ 34'$	Me	$170^\circ\ 19'$	$340^\circ\ 41'$	$315^\circ\ 2'$
5b (TMGNPB)	Me_3Sn	Me_3Sn	386.4	$+16^\circ\ 34'$	Me	$170^\circ\ 29'$	$340^\circ\ 25'$	$315^\circ\ 23'$
6a (TBUNAP)^H	Me_3C	Me_3C	386.1	$+21^\circ\ 16'$	Me	$142^\circ\ 38'$	$337^\circ\ 29'$	$318^\circ\ 49'$
6b (TBUNAP)^H	Me_3C	Me_3C	386.1	$+21^\circ\ 16'$	Me	$152^\circ\ 37'$	$338^\circ\ 21'$	$317^\circ\ 43'$
7 (OCOXAF)	$Ph_2(Me)P^+\ CF_3SO_3^-$	Ph_2P	326.5	$+13^\circ\ 37'$	Ph	$174^\circ\ 2'$	$339^\circ\ 29'$	$316^\circ\ 23'$
8 (OCOXEJ)	$Ph_2(PhCH_2)P^+\ Br^-$	Ph_2P	319.2	$+16^\circ\ 47'$	CH_2Ph	$175^\circ\ 55'$	$340^\circ\ 20'$	$315^\circ\ 23'$
9a (MEXLAC)	$Me_2(O)P$	$Me_2(O)P$	343.2	$+11^\circ\ 10'$	Me	$156^\circ\ 55'$	$340^\circ\ 25'$	$314^\circ\ 42'$
9b (MEXLAC)	$Me_2(O)P$	$Me_2(O)P$	343.2	$+11^\circ\ 10'$	Me	$162^\circ\ 22'$	$339^\circ\ 54'$	$315^\circ\ 34'$
10^F (MEXLEG)	$Ph(t\text{Bu})(O)P$	$Ph(t\text{Bu})(O)P$	347.9	$+1^\circ\ 34'$	*t*Bu	$154^\circ\ 51'$	$338^\circ\ 4'$	$318^\circ\ 3'$
11a (MEXLIK)	$Ph_2(O)P$	$Ph_2(O)P$	337.9	$+14^\circ\ 34'$	Ph	$159^\circ\ 14'$	$340^\circ\ 22'$	$315^\circ\ 7'$
11b (MEXLIK)	$Ph_2(O)P$	$Ph_2(O)P$	337.9	$+14^\circ\ 34'$	Ph	$165^\circ\ 26'$	$340^\circ\ 20'$	$315^\circ\ 10'$
12^G (MEXLOQ)	$Ph_2(S)P$	$Ph_2(S)P$	374.6	$+18^\circ\ 10'$	Ph	$157^\circ\ 14'$	$342^\circ\ 31'$	$312^\circ\ 19'$

(Continued on next page)

TABLE I Data of *peri*-Substituted Naphthalenes 1-$R^e_2R^aX$,8-Y-$C_{10}H^A_6$ *(Continued)*

	TBP character according to Tamao			TBP character according to KDJ				Ratio	
Number	%TBP^e	%TBP^a	%$TBP^{average}$	1.082 · %TBP^{KDJ}	%TBP^{KDJ}	656° 48′ $-\Sigma$(6 angles)	“%TBP”	obtuse:acute angles	Reference
1a	37.8	22.4	30.1	30.1	27.8	1° 8′	4.2	3:3	[23]
1b	41.4	25.1	33.3	33.3	30.8	1° 35′	5.9	3:3	[24]
1c	44.9	27.3	36.1	36.2	33.5	1° 47′	6.6	3:3	[24]
1d	41.7	25.6	33.7	33.9	31.3	1° 46′	6.5	2:4	[24]
1e	44.1	26.3	35.2	35.2	32.6	1° 26′	5.4	4:2^D	[18]
1f	34.5	20.4	27.5	27.4	25.3	1° 0′	3.7	3:3	[11]
1g	38.9	23.2	31.1	31.1	28.8	1° 19′	4.9	3:3	[11]
1h	26.7	15.4	21.1	21.0	19.4	35′	2.2	3:3	[11]
1i	35.0	20.7	27.9	27.9	25.7	1° 3′	3.9	3:3	[11]
1j	37.2	23.0	30.1	30.7	28.4	1° 17′	4.8	3:3	[11]
3a	30.3	17.4	23.9	23.7	21.9	37′	2.2	2:4	[40]
3b	36.6	21.8	29.2	29.2	27.0	1° 10′	4.3	2:4	[40]
4a	36.9	21.8	29.4	29.3	27.1	1° 5′	4.1	2:4	[42]
4b	38.1	22.7	30.4	30.4	28.1	1° 13′	4.5	2:4	[42]
5a	38.9	22.9	30.9	30.8	28.5	1° 5′	4.1	2:4	[42]
5b	38.0	22.3	30.2	30.1	27.8	1° 1′	3.8	2:4	[42]
6a	28.7	16.4	22.6	22.5	20.8	31′	1.9	2:4	[43]
6b	31.5	18.3	24.9	24.8	22.9	45′	2.8	3:3	[43]
7	35.1	20.6	27.9	27.8	25.7	57′	3.5	3:3	[15]
8	37.7	22.3	30.0	30.0	27.7	1° 10′	4.1	2:4	[15]
9a	38.0	23.5	30.8	30.9	28.6	1° 42′	6.3	2:4	[41]
9b	36.4	22.0	29.2	29.2	27.0	1° 22′	5.1	3:3	[41]

10	30.6	17.7	24.2	24.0	22.2	42′	2.6	3:3	[41]
11a	37.8	22.8	30.3	30.3	28.0	1° 20′	5.0	3:3	[41]
11b	37.8	22.7	30.3	30.3	28.0	1° 19′	4.9	3:3	[41]
12	44.6	27.6	36.1	36.4	33.6	2° 0′	7.5	3:3	[41]

[A] For the numbering, see formula **1**.

[B] 2-[(8-dimethylamino-naphth-1-yl)dimethylsilyl]-*N*, *N*,4,4-tetramethyl-1,2,3,3a,4,5-hexahydro-4-sila-5,9b-ethenobenz[*e*]inden-9-amine.

[C] For $R^e = C_{18}H_{24}NSi$, *cf*. reference [23].

[D] One formally obtuse angle insignificantly larger than 109° 28′.

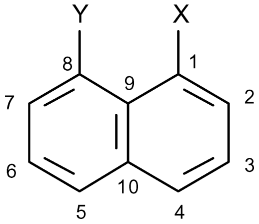
[E] Two independent molecules in the unit cell.

[F] **10a** =**10b**.

[G] **12a** = **12b**.

[H] 3,6-(tBu)$_2$ derivative.

TABLE II Formulae of *peri*-Substituted Naphthalenes 1-X,8-Y-$C_{10}H_6$



1a–1j, **3–12**

	X	Y
1a	$Me_2(C_{18}H_{24}NSi)Si$[23]	Me_2N
1b	$Me_2(4\text{-}O_2NC_6H_4CO\text{-}O\text{-}CH_2CH_2)Si$[24]	Me_2N
1c	$Me_2[3,5\text{-}(O_2N)_2C_6H_3CO\text{-}O\text{-}CH_2CH_2]Si$[24]	Me_2N
1d	$Me_2(2\text{-}O_2NC_6H_4CO\text{-}O\text{-}CH_2CH_2)Si$[24]	Me_2N
1e	$Me_2(PhCH_2)P^+$[18]	Me_2N
1f	$Me_2(Ph)P^+$[11]	Me_2N
1g	$Me(Et)(Ph)P^+$[11]	Me_2N
1h,**i**	$EtPh_2P^+$[11]	Me_2N
1j	$MePh_2P^+$	Me(iPr)N
3	Me_3Si	Me_3Si
4	Me_3Ge	Me_3Ge
5	Me_3Sn	Me_3Sn
6[a]	Me_3C	Me_3C
7	$Ph_2(Me)P^+$	Ph_2P
8	$Ph_2(PhCH_2)P^+$	Ph_2P
9	$Me_2(O)P$	$Me_2(O)P$
10	Ph(tBu)(O)P	Ph(tBu)(O)P
11	$Ph_2(O)P$	$Ph_2(O)P$
12	$Ph_2(S)P$	$Ph_2(S)P$

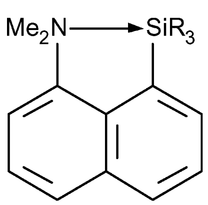
[a] 3,6-(tBu)$_2$ derivative.

interactions[18]), was held responsible for a “small but noticeable distortion of Si [from tetrahedrality] toward the trigonal bipyramidal geometry, with discernible basal and apical substituents,” the $SiMe_2R$ group being a “partially pentavalent silicon substituent.”[24]

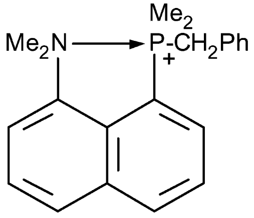
The interpretation revitalizes the question as to whether weak N → P/Si interactions (with N $\cdots$ P/Si distances of ca. 285 ± 35 pm) exist and are amenable to experimental verification. For **1a–j**, a detailed inspection of the partial TBP character argument is mandatory.

DISCUSSION

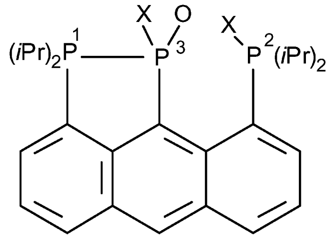
It has become customary to describe the genesis of TBP-hypercoordination by the gradual approach of the fifth ligand Z to the original tetrahedron XY_4. Sterically, the easiest approach of Z is from above one of the triangular planes of the tetrahedron, hence *trans* to the opposite tetrahedral vertex Y^a. The aggregate of the tetrahedron and the approaching atom, $Z \cdot XY_4$, may aptly be called a monocapped tetrahedron,[18,25] regardless of the distance between Z and the plane



2a



2b



X

S **13**

Se **14**

and whether the interaction is attractive, repulsive, or energetically neutral. Attractive forces between the atom in the center of the tetrahedron, X, and Z, presumably increasing with decreasing distance between them, may be expected to induce X to migrate towards the affected plane, thereby increasing the distance to Y^a at the *trans* vertex. When X has reached the plane, the arrangement of the 1 + 5 atoms can be described as a trigonal bipyramid (TBP) with Z and Y^a in apical positions and X in the center of the triangular basal plane formed by the other three ligands, Y^e. If the connecting lines between X and its ligands have the features of covalent bonds, those bonds are either axial[21] (with a *trans* angle Z—X—Y^a of 180°) or equatorial[21] (with an angle Y^e—X—Y^e of 120° between two equatorial ligands and 90° between an apical and an equatorial ligand, Z/Y^a—X—Y^e). The sum of the e/e bond angles, then, will be 360° ($= 3 \cdot 109° \, 28' + 31° \, 36'$), and the sum of the a/e angles on either side of the basal triangle 270° ($= 3 \cdot 109° \, 28' - 58° \, 24'$), so that the sum of all six bond angles of the former tetrahedron will have decreased from $6 \cdot 109° \, 28' = 656° \, 48'$ to $360 + 270° = 630°$. In principle, then, it should be possible to monitor the transition from tetrahedrality to TBP by looking at the deviations of bond angles from tetrahedrality, enlargements as well as decreases. This has lavishly been done, and various methods have been employed (vide infra).

Unfortunately, these procedures suffer from an oversimplification. Even in chemically highly symmetrical molecules, the individual bond angles, as obtained by X-ray crystal structure determination, deviate significantly from ideal behavior, e.g., in $Ph_4P^+ \, N_3^-$, the six C—P—C angles range from 107° 5′ to 110° 56′.[26] It is only their sum that yields an average of 109° 28′, hence perfect tetrahedrality.[27] A recent structure determination of a THF solvate of Ph_5P[28] yielded C—P—C angles, slightly, but significantly, different from those of an old study of the solvent-free compound.[29] In both studies, the C^a—P—C^a angle fell short of 180° by 3° 8′[29] and 1° 13′,[28] respectively. The three C^e—P—C^e angles added to the perfect sum of 360° 0′, but the individual angles ranged from 119° 1′ to 120° 49′.[28] In one of the trigonal pyramids of the TBP, two angles were more acute than 90°, and the third angle was obtuse by 2° 26′; in the other trigonal pyramid vice versa (the small angle was acute by 3° 37′),[28] but again, the sum of all six C^a—P—C^e angles was perfect (540° 0′).[28]

Similar deviations from perfect tetrahedrality are exhibited by the BPh_4^- anion. Its structure is virtually independent of the counter ion (Na^+ , K^+ , Rb^+ , Cs^+),[30–33] but four C—B—C angles exceed 109° 28′ by an average of 2° 57′ while two fall short by 5° 44′ (average). The phenomenon is also shown by $(i\mathrm{Pr})_4P^+$ BPh_4^- (four angles between 111° 55′ and 112° 46′, two 103° 38′)[34]; ironically, it is a little less pronounced in presence of a tetraorgano-ammonium cation of lower symmetry ($PhN^+ Me_2(CH_2Ph)$[10]): the average of the four obtuse angles 111° 36′, of the two acute angles 105° 18′. But again, all six C—B—C angles add to sums deviating from 6 · 109° 28′ by only 20′ or less, the anilinium salt again complying best.

Not surprisingly, this misbehavior is aggravated when different substituents surround the tetrahedral center. Bond lengths and bond angles force geminal substituents at tetrahedral centers into distances that are dramatically shorter than the sum of their van der Waals radii ($d(\mathrm{C}(1)\cdots\mathrm{C}(3))$ = ca. 250 pm in propane[8,35]; $\Sigma r(\mathrm{vdW})[\mathrm{C,C}]$ = 340 pm[36]). Relief from steric or electronic repulsion can be obtained by enlargement of the involved angles, at the expense of other bond angles, so that the sum of all six angles may again be nearly perfect, 6 · 109° 28′. Such phenomena are ubiquitous and most common when the tetrahedral center is bound to hydrogen in addition to more bulky groups. As an example, in 1,1,1,3,3,3-hexaphenyl-propane, $Ph_3C—CH_2—CPh_3$, the C—C—C angle is enlarged to 128° 6′ at the expense of the C—C—H angles (average 104° 40′), while all six angles yield an average of 109° 21′.[37] The geometry of the tetrahedral center and the four covalently bound atoms is then a distorted tetrahedron. Mutatis mutandis, the same can be done for the TBP; the generation of a TBP from a tetrahedron and an approaching ligand is then the transition from a distorted (monocapped) tetrahedron to a distorted TBP (consisting of two distorted trigonal pyramids with a common basal plane). Since the (ideal) tetrahedron is a trigonal pyramid of T_d symmetry, it is trivial that any monocapped distorted tetrahedron can likewise be described as a distorted TBP.[1,7,13,38] The assignment of partial TBP character then becomes dependent of criteria of goodness, and if these are not substantially different for the two alternatives, the distinction becomes meaningless.

If, in a *peri*-disubstituted naphthalene, 1-X,8-Y-$C_{10}H_6$, X is a tetrahedral center, the sterically most favorable arrangement of its substituents will be the conformation in which one group is in the antiperiplanar (*ap*) sector[39] of the naphthalene plane (with respect to the C(1) $\cdots$ C(8) connecting line), and one substituent above and one below the C_{10} plane, residing in the two synclinal (*sc* and –*sc*) sectors[39] as a consequence of the bond angles.[14] The *ap* substituent is then *trans* to Y, so that the arrangement can be described as a monocapped tetrahedron in which the capping atom is the *peri*-bound atom Y. If there is no bond between X and Y, steric repulsion will keep Y at a distance of ca. 285 ± 35 pm. The ubiquitous steric interference between geminal substituents may be envisaged to be greater between the two *sc* groups than between each of them and the *ap* group because of the crowding within the *peri* space. Angle enlargement would provide some relief; if overall tetrahedrality is maintained, it should be compensated by the ± *sc*/*ap* angles. In this case, the arrangement would assume the characteristics of a distorted TBP, although no bonding interaction between the *peri*-bound atoms is involved.

We subjected a number of 1,8-disubstituted naphthalenes 1-X,8-Y-$C_{10}H_6$ with tetrahedral *peri*-substituents X, including **1a–j**, to various tests of partial TBP character. For obvious reasons, we preferentially chose P- and Si-containing substituents[15,40,41]; other group 14 substituents were included.[42,43] In order to maintain the character of the reference compounds as models in which no Y → P/Si bonding interactions are possible, we concentrated on compounds in which Y bears no lone pair that conceivably might interact with X.[40–43] On the other hand, two 8-diphenylphosphino-naphth-1-yl phosphonium cations, 8-Ph_2P-$C_{10}H_6$-P^+ Ph_2R (**7** and **8**),[15] analogs of **1e–j** in which the hard donor group Me_2N has been replaced by the soft donor group Ph_2P, were included. Though, for several reasons, Ph_2P might be a more suitable candidate than Me_2N to engage in a *peri*-donor → acceptor interaction with a phosphonium center,[15] other methods had failed to indicate $P \rightarrow P^+$ hypercoordination.[15]

$$\%\mathrm{TBP}^{\mathrm{a}} = \frac{3 \cdot 109^\circ 28' - \Sigma\vartheta^{\mathrm{a}}}{3 \cdot 109^\circ 28' - 3 \cdot 90^\circ} \cdot 100 \qquad (1)$$

$$\%\mathrm{TBP}^{\mathrm{e}} = \frac{\Sigma\vartheta^{\mathrm{e}} - 3 \cdot 109^\circ 28'}{3 \cdot 120^\circ - 3 \cdot 109^\circ 28'} \cdot 100 \qquad (2)$$

Tamao et al.[44] focussed on distorted tetrahedra in which three angles exceed 109° 28′ and three angles are smaller. Each group was assumed to represent partial TBP character, the latter according to Equation (1), $\Sigma\vartheta^{a}$ being the sum of the three smaller angles. For the obtuse angles, an erroneous equation was published[22]; the actual %TBP$^{\rm e}$ values show that they were calculated with Equation (2). Equation (2)[22] is identical to our equation for the calculation of partial planarization at nitrogen in tertiary amines and their derivatives.[1] TBP^{a} and TBP$^{\rm e}$ reasonably correlated, but %TBP$^{\rm e}$ consistently exceeded %TBP^{a} considerably (e.g., in three examples 95 vs. 88%, 78 vs. 66%,[44] and 88 vs. 66%[22]), indicating that planarization develops faster than its counterpart. This behavior is difficult to reconcile with the model description of a gradual transition and is, in spite of the deviations from perfect TBP character, not observed in Ph_5P.[28] The discrepancy, then, is likely to indicate that other parameters play a significant role, and may raise doubts as to whether the average (%TBP^{a}+ %TBP$^{\rm e}$) : 2 = %TBP$^{\rm average}$ is a meaningful figure for overall bipyramidalization.[1,13] Table I contains %TBP^{a} and %TBP$^{\rm e}$ of **1a–j**, **7**, **8** and the reference compounds as well as their averages %TBP$^{\rm average}$.

Kolb, Dräger, and Jousseaume (KDJ)[45] considered the difference $\Delta\Sigma\vartheta = \Sigma\vartheta^{\rm e} - \Sigma\vartheta^{\rm a}$, $\vartheta^{\rm e}$ and $\vartheta^{\rm a}$ being again the larger and the smaller angles, respectively; $\Delta\Sigma\vartheta = 0$ for the tetrahedron and $\Delta\Sigma\vartheta = 360^\circ - 270^\circ = 90^\circ$ for the TBP. By setting 90° = 100% TBP character, %TBP$^{\rm KDJ}$ is obtained from experimental angles. Table I lists the figures for **1a–j**,**7**, **8** and the reference compounds. %TBP$^{\rm KDJ}$ correlates excellently with %TBP$^{\rm average}$ according to Tamao,[44] but numerically, %TBP$^{\rm average}$ exceeds %TBP$^{\rm KDJ}$ by an average of 8.2%. Table I shows that, throughout, 1.082 · %TBP$^{\rm KDJ}$ and %TBP$^{\rm average}$ are virtually identical. The obvious conclusion is that %TBP$^{\rm KDJ}$ shares with %TBP$^{\rm average}$ the shortcomings for expressing true %TBP character. In fact, the average of the sum of all six bond angles in the reference naphthalenes, 655° 41′, falls short of 6 · 109° 28′ by only 1° 7′ (11′ per angle, i.e., a typical experimental esd value) and thus justifies the description of a distorted tetrahedron without recourse to TBP character, and the high degree of %TBP suggested by Tamao's and KDJ's procedures is grossly misleading. In **1a–j**, the average of the sums of the six angles is smaller by 1° 18′ (13′ per angle), again insignificantly in view of the esd's of the individual angles. The $Me_2N\text{-}C_{10}H_6\text{-}Si/P^+$ compounds can, therefore, not be segregated. Similarly, in **7** and **8**, the average falls short of 6 · 109° 28′ by 1° 0′ (10′ per angle). The average for *all peri*-substituted naphthalenes is 655°

$38' = 656^\circ\ 48' - 1^\circ\ 10'$ (12′ per angle).

$$\%\text{TBP} = \frac{6 \cdot 109^\circ 28' - \Sigma\vartheta}{6 \cdot 109^\circ 28' - 630^\circ} \cdot 100 \tag{3}$$

Since segregation of three obtuse from three acute angles proved to be unsatisfactory, we looked at the integral change of angles from tetrahedrality to the proper trigonal pyramid of the TBP according to Equation (3). The formal TBP character of the non-naphthalenes is 0% within the limits of precision. The non-Me_2N/Ph_2P naphthalene reference compounds yield a small formal TBP character (average 4.2%), which, because of the nature of the *peri*-substituents, cannot be due to incipient Y → X bonding. **7** and **8** deviate even less from tetrahedrality (average 3.8%). The values of **1a–j** yield an average of 4.8%, hence slightly higher, but none of them is outside the range of the reference compounds. Inclusion of these compounds raises the general average to 4.4%.

It is worthwhile to look at some details. Attention has been drawn to the peculiar fact that in **1d**, the Me groups of the $SiMe_2R$ substituent reside in the *sc* sectors, and R in the *ap* sector, but that in **1b**,**c**, one Me and R have changed places[24]; **1a** resembles **1b**,**c**, but one Me is close to orthogonality with respect to the C_{10} plane.[23] Since **1b–d** differ only in an area far from the naphthalene part, this indicates that the energies of the alternative conformations are very similar. This is not surprising, since both Me and R are CH_2—R′ groups, R′ = H and CH_2OCOAr, respectively. The C(sp^3) bond angle at –CH_2— and free rotation around the single bonds permit R′ to stay far away from the congested *peri* area so that in the neighborhood of Si, R is not significantly more bulky than Me. The phenomenon is also met in the *peri*-phosphino-naphthyl phosphonium cations 8-Ph_2P-$C_{10}H_6$-P^+ $Ph_2(CH_2R)$, R = H and Ph.[15] In **7**, one of the Ph groups is the *trans* substituent (angle P ⋯ P—C(Ph) 174° 2′), while in **8**, it is CH_2R (angle P ⋯ P—CH_2 175° 55′). Hence, the feature is no idiosyncrasy of the $Me_2NC_{10}H_6$-silanes.

The interpretation of the distorted monocapped tetrahedron as a distorted TBP *in statu nascendi* was suggested by the fact that three angles were obtuse and three acute.[24] In the BPh_4^- anion and in the cation $(i\text{Pr})_4P^+$ the ratio is 4:2 (Table III).[10,30–34] Inspection of the naphthalene reference compounds reveals eight cases 2:4 and six cases 3:3; in **6a,b** and **9a,b**, both ratios are encountered within one molecule. In the phosphino-phosphonium cations, the ratio is 3:3 in **7** and 2:4 in **8**. Among the four $Me_2NC_{10}H_6$-silanes, there is one exception: In **1d**, the

TABLE III Data of Non-Naphthalene Reference Compounds

Number/formula (CSD-refcode)		d(X · · · Y) [pm]	Splay angle	*trans*-angle	Σ (R^e—X—R^e)	Σ (R^a—X—R^e)
13 (NIKHAR)	$d(P^1—P^3)$	222.7	−10°9′	$P^3 \cdots P^2$—S		
	$d(P^2 \cdots P^3)$	376.5	+23° 58′	176° 36′	328° 1′	328° 45′
14 (NIKHEV)	$d(P^1—P^3)$	223.0	−10°16′	$P^3 \cdots P^2$—Se		
	$d(P^2 \cdots P^3)$	379.3	+21° 26′	176° 4′	327° 55′	328° 49′
$Ph_4P^+ N_3^-$ (XAXJOW)					331° 16′	325° 30′
(iPr)$_4P^+ BPh_4^-$ (DOMLAS)				cation:	332° 10′	324° 43′
				anion:	337° 56′	319° 11′
$PhN^+ Me_2(CH_2Ph)$ (OCITID)				cation:	332° 53′	323° 59′
BPh_4^-				anion:	336° 19′	320° 40′
$Na^+ BPh_4^-$ (ZZZUPI01)				anion:	337° 19′	319° 48′
$K^+ BPh_4^-$ (KTPHEB02)				anion:	337° 48′	319° 22′
$Rb^+ BPh_4^-$ (RBPBOR02)				anion:	337° 10′	319° 57′
$Cs^+ BPh_4^-$ (ZZZURS01)				anion:	336° 43′	320° 22′

Number/formula		TBP character according to Tamao			TBP character according to KDJ				Ratio obtuse:acute angles	Reference
		$\%TBP^{e}$	$\%TBP^{a}$	$\%TBP^{average}$	$1.082 \cdot \%TBP^{KDJ}$	$\%TBP^{KDJ}$	$656^{\circ}\,48' - \Sigma(6\ \text{angles})$	"%TBP"		
13		−1.2	−0.6	−0.9	−0.9	−0.8	+3′	+0.2	2:4	[46]
14		−1.6	−0.7	−1.2	−1.1	−1.0	+5′	+0.3	3:3	[46]
$Ph_4P^+\ N_3^-$		9.0	5.0	7.0	6.9	6.4	+4′	+0.1	3:3	[26]
$(i\mathrm{Pr})_4P^+\ BPh_4^-$	cation:	11.9	6.3	9.1	9.0	8.3	−4′	−0.3	4:2	[34]
	anion:	30.2	15.8	23.0	22.5	20.8	−19′	−1.2	4:2	[34]
$PhN^+\ Me_2(CH_2Ph)$	cation:	14.2	7.6	10.9	10.7	9.9	−4′	−0.3	4:2	[10]
BPh_4^-	anion:	25.0	13.3	19.2	18.8	17.4	−10′	−0.7	4:2	[10]
$Na^+\ BPh_4^-$	anion:	28.2	14.7	21.5	21.1	19.5	−18′	−1.1	4:2	[30]
$K^+\ BPh_4^-$	anion:	29.7	15.5	22.6	22.2	20.5	−20′	−1.2	4:2	[31]
$Rb^+\ BPh_4^-$	anion:	27.7	14.5	21.1	20.7	19.1	−18′	−1.1	4:2	[32]
$Cs^+\ BPh_4^-$	anion:	26.3	13.8	20.1	19.7	18.2	−16′	−1.0	4:2	[33]

ratio is, strictly speaking, 2:4, though one angle falls short of 109° 28′ only by 23′. Even smaller is the (in fact insignificant) deviation from perfect tetrahedrality of one angle that formally confers the ratio of 4:2 to the obtuse vs. acute angles in **1e**. In all, these ratios have to be rated as scatter of angles that add to the sum of 6 · 109° 28′, and a special role emerges neither for **1a–j** nor for **7** and **8**.

An idea about the origin of this scatter is given by two anthracenes with three phosphorus substituents in the *peri* positions 1, 8, and 9, **13** and **14** (see Table III).[46] The 1-and the 9-substituents are connected by a P—P bond whose length of 223 pm enforces a negative splay angle of ca. −10.2°. This deformation gives much relief to the *peri* region around C(8)/C(9). The enormous P(8) ··· P(9) distances of 376.5 pm (**13**) and 379.3 pm (**14**), exceeding the sum of the van der Waals radii $\Sigma r(\mathrm{vdW})[\mathrm{P,P}] = 340$ pm[36] by ca. 11%, are not the consequence of severe crowding, but largely due to the fact that the 9-substituent is towed away by the P(1)—P(9) bond. And lo and behold: %TBP is of insignificant magnitude according to all scales (see Table III).

CONCLUSION

We conclude that the angle deformations at Si in **1a–d** and at P^+ in **1e–j**, **7**, **8** do not reflect incipient Si/P hypercoordination by a N/P → Si/P^+ bond, but are largely the consequence of steric crowding in the *peri* region. The procedures of Tamao et al.[44] and of Kolb, Dräger, and Jousseaume[45] to quantify partial TBP character failed to provide this insight; it is the sum of all six angles that permits recognition of an arrangement of four atoms covalently bound to a central atom as a distorted tetrahedron. Taking into account that the Si atom in **1a–d** and the P atom in **1e–j**, **7**, **8** bear no electronegative substituents, it seems unlikely that at the actual distances $d(\mathrm{N} \cdots \mathrm{Si}) = 292.7$–$304.6$ pm, $d(\mathrm{N} \cdots \mathrm{P}^+) = 282.6$–$295.9$ pm, and $d(\mathrm{P} \cdots \mathrm{P}^+) = 319.2$–$326.5$ pm a potential N/P → Si/P^+ interaction is sufficiently attractive as to significantly reduce the repulsive forces. At least in *peri*-disubstituted naphthalenes, the concept of weak N/P → P/Si bonding may be a chimera.

REFERENCES

[1] Concerning the concept of weak hypercoordinate bonding, cf. Part 14: G. P. Schiemenz, *Z. Naturforsch.*, **61b,** 535 (2006) and references therein.

[2] G. Wittig and M. Rieber, *Liebigs Ann. Chem.*, **562,** 187 (1949).

[3] D. Hellwinkel, *Chem. Ber.*, **98,** 576 (1965); ibid. **99,** 3628 (1966); ibid. **99,** 3660 (1966).

[4] A. Kolomeitsev, V. Movchun, E. Rusanov, G. Bissky, E. Lork, G.-V. Röschenthaler, and P. Kirsch, *Chem. Commun.*, 1017 (1999).

[5] S. Deerenberg, M. Schakel, A. H. J. F. de Kreijzer, M. Kranenburg, M. Lutz, A. L. Spek, and K. Lammertsma, *Chem. Commun.*, 348 (2002).

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

[7] (a) G. P. Schiemenz, *Chem. Listy*, **92,** 269 (1998); (b) G. P. Schiemenz, *Phosphorus, Sulfur, and Silicon*, **163,** 185 (2000).

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

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

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

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

[12] (a) G. P. Schiemenz and C. Näther, *Z. Naturforsch.*, **57b,** 309 (2002); (b) P. M. Dominiak, G. P. Schiemenz, and K. Wozniak, *Polish J. Chem.*, **81,** 663 (2007).

[13] G. P. Schiemenz, *Z. Anorg. Allg. Chem.*, **628,** 2597 (2002).

[14] P. M. Dominiak, S. Petersen, B. Schiemenz, G. P. Schiemenz, and K. Wozniak, *J. Mol. Struct.*, **751,** 172 (2005).

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

[16] P. Kilian, H. L. Milton, A. M. Z. Slawin, and J. D. Woollins, *Inorg. Chem.*, **43,** 2252 (2004).

[17] E.g., (a) C. Brelière, F. Carré, R. J. P. Corriu, M. Poirier, G. Royo, and J. Zwecker, *Organometallics*, **8,** 1831 (1989); (b) F. Carre, M. Chauhan, C. Chuit, R. J. P. Corriu, and C. Reye, *Phosphorus, Sulfur, and Silicon*, **123,** 181 (1997); (c) C. Chuit and C. Reyé, *Eur. J. Inorg. Chem.*, 1847 (1998).

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

[19] (a) E. Fluck and W. Haubold, in: G. M. Kosolapoff and L. Maier (eds.), *Organic Phosphorus Compounds*, **6,** 579-831, p. 638 (1973); (b) W. S. Sheldrick, in: S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, vol. 1 (*The Chemistry of Functional Groups*), (Wiley, Chichester, 1989), pp. 254–260 ; (c) N. A. Barnes, S. M. Godfrey, R. T. A. Halton, I. Mushtaq, and R. G. Pritchard, *Dalton Trans.*, 1346 (2008).

[20] D. Hellwinkel, in: G. M. Kosolapoff and L. Maier (eds.), *Organic Phosphorus Compounds*, vol. 3 (Wiley-Interscience, New York, 1972), p. 233.

[21] S. N. Tandura, M. G. Voronkov, and N. V. Alekseev, *Top. Curr. Chem.*, **131,** 99–189 (1986); ("Apical" refers to the ligands and "axial" to the bonds; cf. G. P. Schiemenz, *Z. Naturforsch.*, **59b,** 807 (2004), note 3.)

[22] N. Kano, A. Kikuchi, and T. Kawashima, *Chem. Commun.*, 2096 (2001).

[23] M. J. Hanson, M. Spiniello, and J. M. White, *J. Organomet. Chem.*, **654,** 3 (2002).

[24] M. Spiniello and J. M. White, *Organometallics*, **27,** 994 (2008).

[25] E.g., C. Brelière, F. Carré, R. J. P. Corriu, G. Royo, and M. W. C. Man, *Organometallics*, **13,** 307 (1994).

[26] R. Haiges, T. Schroer, M. Yousufuddin, and K. O. Christe, *Z. Anorg. Allg. Chem.*, **631,** 2691 (2005).

[27] Cf. G. P. Schiemenz,[1] note 38.

[28] G. Müller and U. J. Bildmann, *Z. Naturforsch.*, **59b,** 1411 (2004).

[29] P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).

[30] A. Yu. Kovalevsky and P. Coppens (State University of New York at Buffalo, NY), private communication to CSD (1999), CCDC 136528.

[31] A. L. Rheingold and J. A. Golen (University of California, San Diego), private communication to CSD (2005), CCDC 281458.

[32] B. Wilde and F. Olbrich (University of Hamburg, Germany), private communication to CSD (2005), CCDC 262677.

[33] J. C. Bryan, *Z. Kristallogr. – New Cryst. Struct.*, **215,** 621 (2000).

[34] H. Schmidbaur, A. Schier, C. M. F. Frazão, and G. Müller, *J. Am. Chem. Soc.*, **108,** 976 (1986).

[35] J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules* (Cornell University Press, Ithaca, NY, 1979), p. 338.

[36] (a) S. S. Batsanov, *Izv. Akad. Nauk, Ser. Khim.*, 24 (1995); *Russ. Chem. Bull.*, **44,** 18 (1995); (b) S. S. Batsanov, *Neorg. Mater.*, **37,** 1031 (2001); *Inorg. Mater.*, **37,** 871 (2001).

[37] J. F. Blount, A. Gutiérrez, and K. Mislow, *J. Org. Chem.*, **47,** 4359 (1982).

[38] Cf. (a) G. Klebe, *J. Organomet. Chem.*, **293,** 147 (1985); (b) H. Schumann, B. C. Wassermann, and F. E. Hahn, *Organometallics*, **11,** 2803 (1992).

[39] Cf. (a) W. Klyne and V. Prelog, *Experientia*, **16,** 521 (1960); (b) J. Rigaudy and S. P. Klesney, International Union of Pure and Applied Chemistry, Organic Chemistry Division, Commission on Nomenclature of Organic Chemistry: *Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H*, (Pergamon Press, Oxford, 1982), p. 484; (c) S. Kane and W. H. Hersh, *J. Chem. Educ.*, **77,** 1366 (2000).

[40] R. Sooriyakumaran, P. Boudjouk, and R. G. Garvey, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **41,** 1348 (1985).

[41] A. Karaçar, M. Freytag, H. Thönnessen, J. Omelanczuk, P. G. Jones, R. Bartsch, and R. Schmnutzler, *Heteroatom Chem.*, **12,** 102 (2001).

[42] J. F. Blount, F. Cozzi, J. R. Damewood, Jr., L. D. Iroff, U. Sjöstrand, and K. Mislow, *J. Am. Chem. Soc.*, **102,** 99 (1980).

[43] J. Handal, J. G. White, R. W. Franck, Y. H. Yuh, and N. L. Allinger, *J. Am. Chem. Soc.*, **99,** 3345 (1977).

[44] K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11,** 2099 (1992).

[45] (a) M. Dräger, *J. Organomet. Chem.*, **251,** 209 (1983); (b) U. Kolb, M. Dräger, and B. Jousseaume, *Organometallics*, **10,** 2737 (1991).

[46] P. Kilian and A. M. Z. Slawin, *Dalton Trans.*, 3289 (2007).