peri-Interactions in Naphthalenes, 14 [1]. Pyramidalization *versus* Planarization at Nitrogen in 8-Dialkylamino-naphth-1-yl Compounds as a Measure of *peri* Bond Formation

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Z. Naturforsch. **61b,** 535 – 554 (2006); received January 23, 2006

The degree of pyramidalization at the N atom of the title compounds permits to distinguish between covalent bond type attraction and other attractive forces. Most so-called coordinative bonds exhibit the features of normal covalent bonds. While such bonds emanating from third or higher period atoms may be rather long, their stretchability is limited, and corresponding interatomic distances are an insufficient criterion for two-electron dative bonds.

Key words: Coordinative (Dative) Bonds, Hypercoordination, Stabilized Silenes, Hydrogen Bonds, van der Waals Radii

Introduction

The interactions between nitrogen and its *peri* neighbour X in 8-dialkylamino-naphth-1-yl (DAN) compounds DAN-X (Fig. 1) are presently not sufficiently understood. Unless substantial attractive forces between N and X are operative, steric repulsion between the substituents enforces distances $d(\mathrm{N}\cdots\mathrm{X})$ exceeding the "natural" *peri* distance (PD) of the undistorted naphthalene skeleton (planar, all angles 120°; PD = *ca*. 250 pm, slightly depending on the nature of X [2 – 5]). In the *proton sponges*, DAN-NR_2, the repulsive forces consist of steric repulsion and electrostatic repulsion (interaction of the lone pairs at the N atoms); the latter manifests itself mainly in the conformation of the R_2N groups with respect to the naphthalene plane [6, 7]. Steric repulsion of the substituents, however, is opposed by the geometry preserving forces (GPF) of the naphthalene skeleton, so that $\mathrm{N}\cdots\mathrm{X}$ distances between *ca*. 265 and *ca*. 310 pm are typical when no attractive forces are operative [3, 8] – distances much shorter than the sum of the respective van der Waals radii, $\sum r_{\mathrm{vdW}}[\mathrm{N},\mathrm{X}]$, which the GPF do not permit to reach even in cases of strong steric hindrance [9]. Consequently, conclusions in favour of *weak bonding interaction* drawn from experimentally found PD $< d(\mathrm{N}\cdots\mathrm{X}) < \sum r_{\mathrm{vdW}}[\mathrm{N},\mathrm{X}]$ are void [5].

Distances considerably shorter than $\sum r_{\mathrm{vdW}}[\mathrm{N},\mathrm{X}]$ but much longer than the sum of the covalent radii,

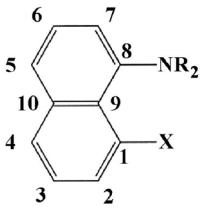

Fig. 1. DAN-X (with numbering scheme).

$\sum r_{\mathrm{cov}}[\mathrm{N},\mathrm{X}]$, have been found in many R_3N/X compounds in which no prohibitive GPF exist. From the fact that $d(\mathrm{N}\cdots\mathrm{X})$ varied greatly, the concept had been derived that a continuous change from *no bond* (expressed by $\sum r_{\mathrm{vdW}}[\mathrm{N},\mathrm{X}]$) to the bond order 1 of covalent bonding (expressed by $\sum r_{\mathrm{cov}}[\mathrm{N},\mathrm{X}]$) exists, and it was even axiomatically assumed that this change obeys a linear relationship from which partial bond orders were calculated [10]. Untenable at least in the case of DAN-X compounds [5, 11], such concepts are popular elsewhere [12] and obviously deserve careful consideration.

Most (if not all) attractive interactions of the two electron type between N and X fall into the category of *dative bonding*; in fact, the symbol of the *dative bond*, $\mathrm{N}\rightarrow\mathrm{X}$, is frequently used. Unfortunately, there is presently no unanimity concerning the properties of *dative bonds*. On the one hand, they are considered a sub-species of covalent bonds [13] which share the characteristic features of the latter, *viz.* a strong resistance against bond stretching and a high

anisotropy (expressed by distinct bond angles) [14]. On the other hand, "normal covalent" N–X bonds and "dative" N → X bonds are increasingly treated as fundamentally different. "Covalent" N–X bonds are written when three atoms are bound to a neutral N atom, all at a distance of $\sum r_{\mathrm{cov}}[\mathrm{N,X}]$. If a fourth atom (or a third atom at formal sp^2-N as in pyridine, Schiff bases *etc.*) is found to reside at a distance $\sum r_{\mathrm{cov}}[\mathrm{N,X}] < d(\mathrm{N}\cdots\mathrm{X}) < \sum r_{\mathrm{vdW}}[\mathrm{N,X}]$, this proximity is frequently called a *dative bond* and described by the symbol of the latter, N → X [15]. Again, such *dative* (or *coordinative*) *bonds* are claimed to be able to adopt any *bond length* between $\sum r_{\mathrm{cov}}[\mathrm{N/O,\ X}]$ and $\sum r_{\mathrm{vdW}}[\mathrm{N/O,X}]$ *ad libitum*, long distances $d(\mathrm{N/O}\cdots\mathrm{X})$ being ascribed to *weak [bonding] interactions* [16]. Such properties would associate *dative bonds* with certain other non-covalent attractive forces such as electrostatic attraction. On the other hand, the frequent and often very detailed discussion of angles implies that – unlike Coulomb attraction – a high degree of anisotropy is assigned to these *dative bonds*.

There exists a host of attractive forces which may reduce $d(\mathrm{N}\cdots\mathrm{X})$ as met in their absence [17]. For various reasons, the very weak and isotropic van der Waals attractive forces can remain out of consideration. A special case is represented by the protonated *proton sponges* and related species. Assisted by the GPF, the energy of their very strong hydrogen bond suffices to compensate the forces of steric repulsion (FSR). Accidentally, the "bond length" of strong $\mathrm{N}\cdots\mathrm{H–N^+}$ and $\mathrm{N}\cdots\mathrm{H–O}$ hydrogen bonds slightly exceeds PD so that such hydrogen bonds fit almost perfectly into the *peri* space and require only a minute distortion of the C_{10} skeleton (*e.g.*, $d(\mathrm{N}\cdots\mathrm{N})[2,7\text{-}Br_2\text{-}1,8\text{-}(Me_2N)_2C_{10}H_4\cdot HBr] = 254.7$ pm [18], $d(\mathrm{N}\cdots\mathrm{O})[\text{DAN-OH}] = 256.9$ pm [19], splay angles of the N–C(1) and the N/O–C(8) bonds $-0.5°$ [20] and $+2.0°$, respectively). On the other hand, their minimum bond length precludes $d(\mathrm{N}\cdots\mathrm{N/O}) <$ PD and negative splay angles in spite of their high bond energy [21].

Other types of attractive forces are not subject to this limitation. Their high bond energy and stout resistance against bond stretching enables covalent bonds between the *peri*-bound atoms X and Y in 1-X-8-Y-substituted naphthalenes to cope with the FSR and the GPF and to enforce interatomic distances $d(\mathrm{X}\cdots\mathrm{Y}) <$ PD [2, 3, 5, 22]. However, such distances are not necessarily restricted to classical covalent bonds. A few cases are known in which $d(\mathrm{X}\cdots\mathrm{Y}) <$ PD and negative splay angles clearly indicate attractive forces while $d(\mathrm{X}\cdots\mathrm{Y}) \gg \sum r_{\mathrm{cov}}[\mathrm{X,Y}]$ looks incompatible with ordinary covalent bonds [23 – 26]. Occasionally, $d(\mathrm{X}\cdots\mathrm{Y})$, though almost equal to or even exceeding PD, falls short of the lower limit of the range observed when attractive forces are absent ($d(\mathrm{X}\cdots\mathrm{Y}) <$ *ca.* 265) [27 – 29] so that obviously some sort of attraction must be operative. *E.g.*, in the pyrocatechol derivative $(\mathrm{DAN})_2\mathrm{Si}(\mathrm{O_2C_6H_4})$, one of the $\mathrm{N}\cdots\mathrm{Si}$ distances (264 and 256) is distinctly shorter than 265 pm and correlates with a formal splay angle of only $+0.7°$ [27]. Here as elsewhere in DAN-X compounds, the formal criteria of *dative bonds* are met so that the concept of easily stretchable dative bonds must be considered.

Dative peri bonds emanating from the N atom of DAN-X may either respect the octet rule (*e.g.*, N→B/Al) or be *hypercoordinate dative bonds* (*e.g.*, N→Si/P) [30]. Classification as *dative bonds* is not restricted to N→X with X having a lower electronegativity than N, the N→O bond of amine oxides being the prototype of the *dative bond* [31] and its symbol → having been applied to an N–N bond as well ($\mathrm{Me_3N{\rightarrow}NCH_2R}$ [32]). $\mathrm{N^+}$–C bonds of quaternary ammonium salts, therefore, cannot be logically excluded, in particular not the $\mathrm{N^+}$–C bond with *peri*-bound C in $[\text{DAN-C}]^+$ salts whose reactions comply with Haaland's definition of *dative bonds* [33].

Previous studies of N/X bonding interactions in DAN-X compounds and elsewhere have mainly focussed either on $d(\mathrm{N}\cdots\mathrm{X})$ or on the geometry around X (planar *vs.* tetrahedral coordination around B/Al, tetrahedral *vs.* trigonal-bipyramidal (TBP) around P/Si, *etc.*). Some serious shortcomings [34] and the lack of generality induced us to turn our attention to a property which so far has not been exploited, planarization *vs.* pyramidalization at the N atom. Our discussion is largely based on material deposited in the Cambridge Crystal Data Centre or elsewhere as *Supplementary Information* to published papers.

Results and Discussion

In quaternary ammonium salts, the coordination around the $\mathrm{N^+}$ atom is tetrahedral. When different groups are attached to the N atom, the tetrahedron is slightly distorted, but the sum of the six $\mathrm{C–N^+–C}$ angles is still almost precisely $6\cdot 109.47° = 656.8°$. This is the case even in cations of 1-azonia-acenaphthene structure, hence *peri*-N/C substituted naphthalenes in which the N atom and the C atom are connected

Table 1. 8-Dialkylamino-naphth-1-yl compounds DAN-X.

Entry	Formula	Bond N→X[b]		d(N···X)	Splay angle	Angles C–N–C		Angles C–N–X	Lit.
	DAN-X[a]	a priori	result	[pm]	[°]	subset A [°]	PL [%]	subset B[c] [°]	
1	$[DAN\text{-}CEtMe]^+\ BPh_4^-$	+	+	159.9	−31.6	327.6	−2.7	329.1+	[22]
2	$[DAN\text{-}C(C_{14}H_{10})]^+BF_4^-$ [d]	+	+	171.9	−23.8	326.4	−6.3	330.3+	[22]
		+	+	171.9	−23.5	326.7	−5.4	329.9+	
3	$(DAN)_2C(H)OH$	–[e]	–	287.6	+10.1	334.9	20.6	318.4–	[1,2]
		–[f]	–	286.6	+10.8	334.4	19.0	320.2–	
4	(S)-DAN-C(H)(Ph)OH	–[e]	–	287.6	+10.8	336.8	26.5	317.1–	[1]
5	(R)-DAN-C(H)(Ph)OH	–[f]	–	284.8	+7.5	340.2	37.3	313.3–	[1]
6	$DAN\text{-}C(C_3H_5)_2OH$[g]	–	–	314.1	+19.5	333.4	15.8	320.3–	[1]
7	$(DAN)_2(CH)_2(SiR_2)_2$[h]	–	–	297.5	+10.2	339.4	34.8	313.7–	[39]
		–	–	298.5	+8.0	339.0	33.5	313.7–	
8	DAN(B)-Br	–	–	299.1	+9.4	343.3	47.2	309.5–	[4]
9	$DAN\text{-}NMe_2$	–	–	279.2	+6.7	346.9	58.5	[i]	[6]
						347.2	59.5	[i]	
10	$DAN\text{-}NMe_2$	–	–	[i]	+6.3	346.4	57.0	309.6–	[7]
						347.1	59.2	313.2–	
11	$2,7\text{-}Me_2DAN\text{-}NMe_2$	–	–	274.9	+6.3	352.5	76.3	296.7–	[98]
						352.8	77.2	296.7–	
12	$2\text{-}(HO)Ph_2C\text{-}DAN\text{-}NMe_2$	–	–	292.1	+9.3	N(1): 350.4	69.6	238.5–	[99]
						N(8): 335.7	23.1	318.3–	
13	$2,7\text{-}[(HO)Ph_2C]_2\text{-}DAN\text{-}NMe_2$	–	–	292.1	+4.4	350.1	68.7	301.6–	[99]
						350.6	70.3	239.5–	
14	$2,7\text{-}(EtOOC)_2DAN\text{-}NMe_2$	–	–	276.0	+7.2	353.3	78.8	294.8–	[98]
						353.0	77.8	295.4–	
15	$2,7\text{-}Cl_2DAN\text{-}NMe_2$[j]	–	–	276.1	+7.8	353.0	77.8	295.9–	[100]
						352.8	77.2	296.1–	
16	$2,7\text{-}Cl_2DAN\text{-}NMe_2$[j]	–	–	277.5	+8.4	353.3	78.8	295.6–	[100]
						352.9	77.5	296.2–	
17	$2,7\text{-}Br_2DAN\text{-}NMe_2$	–	–	274.8	+7.0	354.2	81.6	294.1–	[18]
						354.4	82.3	292.8–	
18	$2,7\text{-}I_2DAN\text{-}NMe_2$	–	–	282	+10.7	353.4	79.1	281.9–	[98]
						359.9	99.7	284.6–	
19	$4,5\text{-}(MeO)_2DAN\text{-}NMe_2$	–	–	277.3	+4.1	340.9	39.6	309.6–	[101]
						343.2	46.8	312.2–	
20	$2,7\text{-}(MeO)_2DAN\text{-}NMe_2$	–	–	275.6	+6.7	346.4	56.9	303.9–	[102]
						345.9	55.5	306.6–	
21	$4,5\text{-}(Me_2N)_2DAN\text{-}NMe_2$	–	–	274.5	+4.8	344.2	50.0	[i]–	[103]
						344.7	51.6	[i]–	
22	$2,7\text{-}(Me_2N)_2DAN\text{-}NMe_2$	–	–	277.0	+4.7	355.6	86.1	287.3–	[103]
						356.8	89.9	290.2–	
				for comparison: N(2):		340.4	38.0		
				for comparison: N(7):		338.6	32.3		
23	$2,7\text{-}(C_4H_8N)_2DAN\text{-}NMe_2$[k]	–	–	[i]	+9.4	357.6	92.4	285.9–	[103]
24	$2,7\text{-}(MeS)_2DAN\text{-}NMe_2$	–	–	283.0	+11.0	352.4	75.9	297.3–	[98]
						359.7	99.1	275.7–	
25	$2,7\text{-}(Me_3Si)_2DAN\text{-}NMe_2$	–	–	292.5	+8.5	350.4	69.6	300.7–	[98]
						355.3	85.3	248.9–	
26	DAN-OH	–	–	256.9	+2.0	335.6	22.8	[i]–	[19]
27	$DAN\text{-}N^+HMe_2$[l]	–	–	261.0	+2.7	334.8	20.3	[i]–	[104]
						335.8	23.4	[i]–	
28	$2,7\text{-}Cl_2DAN\text{-}N^+HMe_2\ Br^-$	–	–	256.1	+0.7	342.7	45.3	311.8–	[100]
29	$2,7\text{-}Br_2DAN\text{-}N^+HMe_2\ Br^-$	–	–	254.7	−0.5[m]	342.9	45.9	311.6–	[18]
30	DAN-CO-Me	?	–	255.7	+2.1	338.3[n]	31.3	[i]	[42]
31	DAN-COOH	?	–	260.6	+3.8	339.6[o]	35.4	[i]	[42]
32	DAN-CO-OMe	?	–	259.4	+1.3	338.3[p]	31.3	[i]	[42]

Table 1 (continued).

Entry	Formula	Bond N→X[b]		d(N···X)	Splay angle	Angles C–N–C		Angles C–N–X	Lit.
	DAN-X[a]	a priori	result	[pm]	[°]	subset A [°]	PL [%]	subset B[c] [°]	
33	DAN-CO-NMe_2	?	–	[i]	+5.5	337.9[q]	30.1	316.4–	[43]
34	DAN-CO-$N(CHMe_2)_2$	?	–	[i]	+8.9	336.6[r]	26.0	317.7–	[43]
35	α-$C_{10}H_7$-NMe_2 →$AlMe_3$	?	+	215.7	[s]	325.5	−9.2	330.8+	[44]
36	DAN-AlH_2	?	+	211.8	−14.4	329.5	3.5	327.2+	[45]
37	DAN-$AlMe_2$	?	+	206.3	−14.3	328.5	0.3	328.4+	[46]
38	DAN-$AlEt_2$[t]	?	+	207.1	−14.8	329.4	3.2	327.4+	[44]
		?	+	206.9	−14.8	328.5	0.3	328.2+	
39	DAN-$AlCl_2$	?	+	201.6	−16.0	328.8	1.3	327.8+	[45]
40	DAN-$GaCl_2$	?	+	207.1	−14.2	328.5	0.3	328.1+	[45]
41	DAN-$InCl_2$	?	(+)	240.5	−5.7	330.6	7.0	326.3?	[45]
42	2 $[(DAN)_2SiH]^+$ $I_8{}^{2-}$	?	+	206.2	−19.5	329.6	3.8	326.4+	[50]
				208.6	−23.0	329.6	3.8	326.7+	
43	DAN-$SiMe_2R$[u]	?	–	304.6	+8.7	335.4	22.2	[i]–	[41]
44	DAN-$Si^1(SiMe_3)$=$C(SiMe_3)_2$[v]	?	+	206.9	−14.9	330.1	5.4	326.6+	[55]
45	$(DAN)_2PH$	–	–	279.1	+6.6	336.7	26.3	318.0–	[105]
		–	–	270.2	+3.4	340.0	36.7	314.8–	
46	DAN(E)-PPh_2	–	–	280.3	+6.9	332.2	12.0	321.1–	[8]
47	$(DAN)_3P$	?	–	282.0	+6.8	337.7	29.4	316.8–	[106]
		?	–	282.8	+7.4	336.4	25.3	319.5–	
		?	–	288.5	+6.0	338.3	31.3	317.1–	
48	$(DAN(E))_3P$	?	–	289.7	+7.6	337.2	27.8	322.1–	[107]
		?	–	290.2	+7.7	339.0	33.5	314.1–	
		?	–	292.0	+8.5	338.5	32.0	314.3–	
49	DAN-$P(C_{12}H_8)_2$[w]	–	–	281.0	+3.2	332.4	12.7	[i]–	[70]
50	DAN-$P(O)(OEt)_2$	?	–	286.9	+8.6	336.3	25.0	319.6–	[71]
51	$(DAN)_3As$	?	–	280.7	+6.2	335.6	22.8	320.3–	[72]
		?	–	281.3	+5.9	337.7	29.4	317.0–	
		?	–	285.5	+2.4	335.7	23.1	320.5–	
52	DAN-$Sb(C_6H_4$-Me-4$)_2$	?	–	283.0	+3.4	337.9	30.1	317.4–	[29]
53	$(DAN)_3P^+H$ Cl^-	?	–	277.5	+7.4	333.6	16.5	322.5–	[106]
		?	–	278.1	+7.6	333.9	17.4	322.0–	
		?	–	288.2	+10.3	333.5	16.1	322.7–	
54	$(DAN)_2P^+(H)Ph$ Br^-	?	–	270	+4.6	331.9	11.2	323.8–	[69]
		?	–	274	+7.1	334.5	19.3	321.8–	
55	DAN-P^+Me_2Ph $BPh_4{}^{-x}$	–	–	293.9	+5.8	332.8	13.8	322.5–	[4]
56	DAN-$P^+Ph_2(CH_2Ph)$ Br^-	?	–	283	+4.8	332.4	12.7	323.6–	[108]
57	DAN-$P^+(Et)(Me)Ph$ $BPh_4{}^{-y}$	–	–	289.1	+6.5	332.2	12.0	323.5–	[4]
58	DAN(Me*i*Pr)-P^+Ph_2Me $BPh_4{}^{-z}$	–	–	295.9	+7.0	337.8	29.8	318.0–	[4]
59	DAN-P^+Ph_2Et $BPh_4{}^{-j,A}$	–	–	289.3	+7.3	332.2	12.0	323.6–	[4]
		–	–	295.3	+7.8	334.5	19.3	320.8–	
60	DAN-$P(O_2C_6H_4)_2$[B]	+	+	213.2	−11.5	326.5	−6.0	330.3+	[3]
61	DAN-SiF_3	?	+	231.8	−6.1	328.5	0.3	328.3+	[23]
62	$[DAN\text{-}SiF_4]^-$ $K^+ \cdot$ 18-crown-6	?	+	221.3	−8.8	327.5	−2.8	329.3+	[24]
63	$(DAN)_2AlEt$	?	+	224.4	−15.5	328.2	−0.6	327.9+	[44]
		?	+	226.5	−19.0	329.1	2.2	327.4+	
64	DAN-CH-$C(CO\text{-}O)_2CMe_2$	+	+	165.1	−28.0	330.8	7.6	326.0+	[25]
65	DAN-CH=$C(COPh)_2$	?	–	267.9	+4.3	341.2	40.5	312.3–	[25]
66	DAN-CH=$C(CN)_2$	?	–	241.3	−3.5	340.8	39.1	314.3–	[25]
67	DAN-Se-Cl	?	–	217.4	−11.7	334.8	20.3	321.8–	[88]
68	DAN-Se-I	?	–	224.2	−10.4	335.3	21.8	321.3–	[88]
69	DAN-Te-Br	?		239.5	−6.1	332.5	13.0	324.2–	[89]
70	DAN-Te-S-CS-NEt_2	?	–	250.5[C]	−3.3	333.9	17.4	322.7–	[88]
71	DAN-Te-Ph	–	–	271.3	+1.9	337.7	29.4	[i]–	[89]
72	$(DAN\text{-}Te\text{-})_2$	–	–	269.9	+1.7	336.9	26.9	[i]–	[89]
		–	–	274.3	+1.7	337.2	27.8	[i]–	
73	DAN-$Si(H)[O_2(CMe_2)_2]$[D]	?	?	233.9	−7.9	331.7	10.5	326.1?	[26]

Table 1 (continued).

Entry	Formula DAN-X[a]	Bond N→X[b] a priori	Bond N→X[b] result	d(N···X) [pm]	Splay angle [°]	Angles C–N–C subset A [°]	PL [%]	Angles C–N–X subset B[c] [°]	Lit.
74	$(DAN)_2Si(O_2C_6H_4)^B$	+?	(+)	256	+0.7	329.7	4.1	326.9?	[27]
		–?	–	264	+3.3	331.7	10.4	324.7–	
75	$(DAN\text{-}SiMe_2\text{-})_2O$	?	–	284.9	+2.0	332.9	14.2	[i]–	[28]
		?	–	285.1	+3.2	334.5	19.3	[i]–	
76	$[DAN\text{-}Si(CH_2)_3\text{-}]_2O^E$	?	–	261.4	−0.7	334.1	18.0	[i]–	[28]
		?	–	262.1	−1.0	335.0	21.0	[i]–	
77	$DAN\text{-}SbCl_2(C_6H_4\text{-}Me\text{-}4)_2$	?	–	265.8	+1.0	331.9	11.1	–	[29]

[a] Bonds N→X not indicated. DAN: $R_2N = Me_2N$, DAN(E): $R_2N = Et_2N$, DAN(B): $R_2N = (PhCH_2)_2N$, DAN(Me*i*Pr): $R_2N = (Me)(Me_2CH)N$. – [b] + = yes, – = no, ? = in question. – [c] + = bond angle, – = no bond angle, ? = type in question. – [d] $C_{14}H_{10}$ = (Z)-stilbene-2,2'-diyl; 2 molecules. – [e] Hydrogen bond N···H–O possible. – [f] No hydrogen bond N···H–O possible. – [g] C_3H_5 = cyclopropyl. – [h] R = $SiMe_3$, $(CH)_2(SiR_2)_2$ = 1,1,3,3-tetrakis(trimethylsilyl)-1,3-disila-cyclobutane-2,4-diyl. – [i] Not available. – [j] 2 molecules. – [k] C_4H_8N = 1-pyrrolidyl. – [l] Anion: $C_{24}H_{17}N_6O_{12}S_2^-$ (see Malarski *et al.* [104]). – [m] Deviation of the sum of the bay angles from 360° smaller than the sum of the esd's. – [n−r] For comparison: [n] ∑(C–$C_{carbonyl}$–C/O) = 358.7° (PL = 95.9%). – [o] ∑(O–C–C/O) = 359.4° (PL = 98.1%). – [p] ∑(O–C–C/O) = 359.3° (PL = 97.8%). – [q] ∑(C–N–C)[amide] = 359.5°, ∑(C/O–C–O/C)[amide] = 359.5° (PL = 98.4%). – [r] ∑(C–N–C)[amide] = 360.0°, ∑(C/O–C–O/C)[amide] = 359.6° (PL = 98.7%). – [s] Only N–C(1)–C(9) (119.9°) and C(1)–C(9)–C(8) (124.4°) available, indicating a positive splay angle. – [t] CCDC 230 189 (2 molecules); slightly different data in CCDC 230 181. – [u] R = $C_{17}H_{20}NSi$ (see Hanson *et al.* [41]). – [v] Planarization at the ylidic C atom: PL = 96.4%, at Si[l]: 54.1% (sum of all 6 angles N/C–Si–C/Si: 656.8 – 7.8°). – [w] $C_{12}H_8$ = 2,2'-biphenylylene. [x−A] Tetrahedrality at P^+: sum of all 6 angles: [x] 656.8 – 1.0°, [y] −1.3°, [z] −1.2°, [A] −1.0°/−0.6°. – [B] $O_2C_6H_4$ = *ortho*-phenylene-dioxy. – [C] PD = 256 pm. – [D] $O_2(CMe_2)_2$ = –O–CMe_2–CMe_2–O–. – [E] $(CH_2)_3$ = –CH_2–CH_2–CH_2–.

by a covalent bond. The GPF render the angle C(8)–N^+–C_{peri} much more acute, but other angles widen correspondingly so that the sum remains virtually unchanged (Table 1, entries 1, 2).

On the other hand, the C–N–C angles of tertiary amines consistently lie between 109.47° (tetrahedral) and 120° (planar): The nitrogen atom is partially planarized. As a rule, the phenomenon is more pronounced in dialkyl-arylamines (including DAN compounds) than in trialkylamines such as benzyl-dimethylamines and analogous ferrocenes [35], but it is not restricted to amines $ArNR_2$ and therefore cannot simply be ascribed to engagement of the lone pair at N in resonance with Ar [36]; the sum of the three C–N–C angles varies considerably so that presumably a variety of parameters is responsible for the angle widening. Nevertheless, it is general, so that bond formation and possibly even "weak bonding interactions" should be identifiable by the decrease of the degree of planarization (PL) as defined in equation (1).

$$\mathrm{PL}(\%) = \frac{\sum(\text{C-N-C}) - 3\cdot 109.47^\circ}{3\cdot 120^\circ - 3\cdot 109.47^\circ}\cdot 100 = \frac{\sum(\text{C-N-C}) - 328.4^\circ}{31.6}\cdot 100 \qquad (1)$$

In DAN-X, besides the three C–N–C angles three angles C–N–X exist which are bond angles in cases of a *peri* bond N–X, no-bond angles in cases where a *peri* bond is absent, and have an ill-defined status in cases of "weak bonding interactions" or any other attractive forces than covalent *peri* bonds. In order to render the six tetrahedral angles of the quaternary ammonium salts comparable with the angles of the tertiary amines, either the sum of all six C–N–C/X angles of the amines must be correlated with the sum of the six C–N^+–C angles of the salts, or the latter sum must be divided into two subsets, the three C–N^+–C angles which correspond to the C–N–C angles of the amines (angle subset A) and the three C–N^+–C_{peri} angles which correspond to the C–N–X angles (angle subset B). Of the two possibilities, only the second is feasible. In the amines, the three C–N–C angles (subset A) add to more than $3\cdot 109.47^\circ = 328.4^\circ$ because of the partial planarization. In all cases of no N···X *peri* bond, the C–N···X angles (subset B) accidentally add to a sum smaller than but often similar to 328.4°. The deviations from 328.4° in the two subsets therefore largely cancel each other, so that the information contained in PL is blurred. Fortunately, both subsets of C–N^+–C angles add very well to 328.4° in spite of the fact that the angle $C(8)_{DAN}$–N^+–C_{peri} is much smaller than 109.47°. The deviations from ideal behaviour are of the same magnitude as in the subsets of three tetrahedral angles in tetraalkylammonium salts which are obtained when the three largest and the three smallest angles are grouped together (see Table 3).

Clear-cut cases provide an insight into the utility and the limits of the method.

Table 2. Other compounds with potential N→X interaction (Ar-X = 2-Me_2NCH_2-6-R-C_6H_3-X, Fc-X = C_5H_5→Fe← (2-Me_2NCH_2)-C_5H_3X).

Entry	Formula[a]	Bond N→X in question		d(N···X)	Angles C–N–C		Angles C–N–X[b]	Lit.
		Type	result[c]	[pm]	subset A [°]	PL [%]	subset B [°]	
78	Me_2N-$(CH_2)_3$-$AlMe_2$	N→Al	+	203.9	328.3	−0.3	328.3	[46]
79	Me_2N-$(CH_2)_3$-Al$(CH_2)_5$[d,e]	N→Al	+	205.7	327.1	−1.3	329.5	[46]
80	Me_2N-$(CH_2)_3$-B$(CH_2)_5$[d,f]	N→B	+	168.2	328.1	−0.9	328.5	[46]
		N→B	+	168.4	327.6	−2.5	328.9	
81	Me_3NGaH_3	N→Ga	+	208.1	327.3	−3.5	329.4	[47]
82	$HC(C_2H_4)_3N{\cdot}GaH_3$[g]	N→Ga	+	206.3	324.7	−11.7	332.0	[48]
83	2-$Me_2NCH(Me)C_6H_4GaCl_2$[h]	N→Ga	+	204.9	329.8	+4.4	326.7	[46]
84	$[Ar_2SiH]^+$ $CF_3SO_3{}^-$[i]	N→Si	+	205.2	327.7	−2.2	328.8	[54]
		N→Si	+	207.2	327.1	−4.1	329.0	
85	Ar-SiF_2Me	N→Si	+	234.6[j]	326.8	−5.1	[k]	[82]
86	Ar-$Si^I(SiMe_3)$=$C(SiMe_3)_2$[l]	N→Si^I	+	200.4	328.8	+1.3	328.0	[56]
87	Ar-$Si^I(SiMe_3)$=$C(SiMe_3)_2$[m]	N→Si^I	+	203.5	327.9	−1.6	328.8	[57a]
	(6-R = $CH_2N^{II}Me_2$)	N^{II} →Si^I	–		332.2	+12.0[n]		
88	Ar-Si(Ph)$(O_2C_6H_4)$[o]	N→Si	+	216.3	327.7	−2.2	328.9	[83]
89	$[Ar\text{-}Si(O_2C_6H_4)_2]^-$[o,q]	N→Si	+	217.3	326.6	−5.7		[35a]
	(6-R = $CH_2N^{II}Me_2$)	N^{II} →Si	–	479.2	331.6	+10.1[p]		
90	$[Ar\text{-}Si(O_2C_6H_4)_2]^-$[o,q]	N→Si	+	215.7	325.2	−10.1	331.4	[85]
91	Ar-$Si^-(O_2C_6H_4)_2$	N→Si	+	208.7	326.0	−7.6	330.6	[86]
	(6-R = $CH_2N^+Me_2H$)[o]	(Me_2HN^+:)	–	352.1	324.1	−13.7	317.7	
92	Ar_2SiCl_2	N→Si	+	229.1	326.9	−4.6	329.5	[35b,c]
		N→Si	–	449.3	331.3	+9.3		
93	Ar_2Se	N→Se	–	[k]	335.2	+21.5		[88]
		N→Se	–	[k]	334.2	+18.4		
94	Ar-S^+ $PF_6{}^-$ (6-R = CH_2NMe_2)	N→S	–	206.3	335.5	+22.5	320.9	[92]
95	Ar-Te-I	N→Te	–	236.6	334.0	+17.7	322.6	[90]
96	Ar_2Te	N→Te	–	304.8	335.6	+22.8		[90]
		N→Te	–	314.5	333.5	+16.1		
97	Ar_3As	N→As	–	293.6	335.2	+21.5	318.8	[72]
		N→As	–	296.1	335.5	+22.5	317.7	
		N→As	–	303.0	334.5	+19.3	318.4	
98	Ar_3Sb[r]	N→Sb	–	303	335.4	+22.2	318.2	[72]
		N→Sb	–	304	332.6	+13.3	322.3	
		N→Sb	–	304.1	332.3	+12.3	322.2	
99	Ar_3Sb[r]	N→Sb	–	297.4	334.3	+18.7		[35f]
		N→Sb	–	297.6	336.3	+25.0		
		N→Sb	–	302.2	334.6	+19.6		
100	Ar-Sb$(C_6H_4CH_2N^+Me_3\text{-}2)_2$ $2I^-$	N→Sb	–	281.7	331.5	+9.8		[35f]
101	2-$Me_2NCH(Me)$-C_6H_4-SbR_2 $2I^-$ (R = $C_6H_4CH(Me)N^+Me_3$-2)	N→Sb	–	280.4	338.9	+33.2		[35f]
102	$[2\text{-}Me_2NCH(Me)\text{-}C_6H_4]_3Sb$[s]	N→Sb	–	292.0	338.3	+31.3		[35f]
		N→Sb	–	298.8	338.1	+30.7		
		N→Sb	–	[k]	333.7	+16.8		
103	$Fc_2Si(OH)_2$	N→Si	–	351.4	331.5	+9.8	315.7	[35d]
		N→Si	–	364.6	331.9	+11.1	315.0	
104	Fc_2SiCl_2	N→Si	–	354.7	333.5	+16.1	318.2	[35e]
		N→Si	–	403.2	331.3	+9.2	310.3	
105	Fc_2SiMe_2	N→Si	–	376.8	333.5	+16.1	316.2	[35e]
		N→Si	–	415.9	332.3	+12.3	308.7	

[a] N–X bonds not indicated; 6-R = H, unless otherwise indicated. – [b] In cases of large d(N···X) not determined. – [c] + = yes, – = no. – [d] $(CH_2)_5$ = pentane-1,5-diyl. – [e] Tetrahedrality at Al: sum of all six angles 656.8 – 2.6°. – [f] Two molecules. Tetrahedrality at B: sum of all six angles 656.8 −0.4/ − 0.4°. – [g] $HC(C_2H_4)_3N$ = quinuclidine. For comparison: $[(H_2(t\text{Bu})N)_2GaH_2]^+$ Cl^-: d(N–Ga) = 201.6/201.8 pm [109]. – [h] Tetrahedrality at Ga: sum of all six angles 656.8 – 3.7°. – [i] Notwithstanding the low precision of the H–Si–C/N angles, TBP geometry at Si is perfect except a deviation of the a/a (N–Si–N) angle from linearity by 8.8° [54]. – [j] Klebe [82], p. 37: 235.6 pm. – [k] Not available. – [l] Perfect tetrahedrality at N: Sum of all six angles 656.8°. Planarization at the ylidic C atom: PL = 97.8%, at Si^I: PL = 48.1% (sum of all N/C–Si^I–C/Si angles 656.8 – 6.1°). – [m] Perfect tetrahedrality at N: Sum of all six angles 656.7°. The C-Si^I-C/Si angles correspond to a planarization of PL = 63.6%. The sum of all six angles C/N-Si^I-C/Si falls short of perfect tetrahedrality by 10.3°. Planarization at the ylidic C atom: PL = 99.7%. – [n] 13.4% by internal reference. – [o] $O_2C_6H_4$ = *ortho*-phenylenedioxy. – [p] 15.0% by internal reference. – [q] Cation $[(Ph_3P)_2N]^+$. – [r] Entries 98, 99: Different space groups. – [s] d(N···Sb) has been called a *bond length*, the angles C–Sb···N *bond angles* [35f].

Table 3. Selected salts $R_4X^+ Y^-$: Sums of the three largest and the three smallest angles C–X^+–C (for comparison).

Entry	Formula	Angle	∑(C–X^+–C) [°] largest angles	smallest angles	Lit.
106	$Me_4N^+ HF_2^-$	C–N^+–C	328.8	328.1	[110]
107	$Me_4N^+ H_2F_3^-$	C–N^+–C	328.9	327.9	[110]
108	Et_4N^+ Ph-TeI_4^-	C–N^+–C	332.6	324.2	[111]
109	$Ph_4P^+ N_3^-$	C–P^+–C	331.3	325.5	[37]

Model compounds

Formally symmetrical ammonium cations of the $C(sp^3)_4N^+$ type should provide an insight into the accuracy of tetrahedrality. In two salts of the Me_4N^+ cation (Table 3, entries 106, 107), the three smallest C–N–C angles add to $328.4 - 0.3°$ ($-0.5°$), the three largest angles to $328.4 + 0.4°$ ($+0.5°$), all six angles to $656.8 + 0.1°$ ($\pm 0.0°$). In a Et_4N^+ salt (Table 3, entry 108), the deviations are significantly greater (three smallest angles $328.4 - 4.2°$, three largest angles $328.4 + 4.2°$), but the total sum is again 656.8°. Ph_4P^+ is a symmetrical cation in which the role of an aryl group at the onium centre can be studied. In its azide [37] (Table 3, entry 109), the three smallest/largest C–P–C angles add to $328.4 - 2.9°$ and $+2.9°$, respectively, so that the total sum is again perfect. $PhN^+Me_2(CH_2Ph)$ BPh_4^- is a fairly close analog of DAN-C salts with a N^+–C_{peri} bond [22]; the Me–N^+–Me/C(sp^2) angles correspond to the Me–N^+–Me/C(8) angles (subset A) and the H_2C–N^+–Me/C(sp^2) to the C_{peri}–N^+–Me/C(8) angles (subset B) of the latter. The salt deviates only little from perfect tetrahedrality (subset A: $328.4 + 1.2°$, PL = 3.8%; subset B: $328.4 - 1.2°$, all angles 656.8°) [38].

DAN-C compounds with a N^+–C_{peri} bond

The data of DAN-C compounds with a N^+–C_{peri} bond fit well into this frame. In 2-ethyl-1,1,2-trimethyl-1-azonia-acenaphthene [22] (Table 1, entry 1), subset A (three Me–N^+–Me/C(8) angles) amounts to $328.4 - 0.9°$, subset B (the C_{peri}–N^+–Me/C(8) angles) to $328.4 + 0.7°$, their sum to $656.8 - 0.2°$. In two independent molecules of a 1-azonia-acenaphthene with an elongated N^+–C_{peri} bond [22] (Table 1, entry 2), the respective data are $328.4 - 2.0/-1.7°$ (subset A), $328.4 + 1.9/+1.5°$ (subset B) and $656.8 - 0.1/-0.2°$. In either case, only subset A is relevant for comparison with DAN-X compounds containing a non-coordinating N atom; in both cases, the sum of the angles is slightly *smaller* than 328.4°.

DAN-C compounds without a N^+–C_{peri} bond

Three DAN-carbinols [1, 2] (Table 1, entries 3 – 6) provide a countercheck of an uncoordinated Me_2N group. The DAN groups of $(DAN)_2CH(OH)$ are diastereotopic because of restricted rotations [1, 2]. DAN-CH(Ph)(OH), formally a racemate, is in fact a 1 : 1 mixture of diastereomers (again due to restricted rotations) [1], so that the three structures contain five different DAN groups. The splay angles of the N–C(8) and the C_{peri}–C(1) bonds range from $+7.5°$ to $+19.5°$. The distances $d(N\cdots C_{peri})$ exceed PD significantly as a consequence of steric hindrance between the *peri* substituents. Angle subset A amounts to $328.4 + 8.4°$ (PL = 26.6%) for the (S)-enantiomer and $328.4 + 11.8°$ (PL = 37.3%) for the (R)-enantiomer of DAN-CH(Ph)(OH), to $328.4 + 6.0°/+6.5°$ (PL = 19.0/20.6%) for the DAN groups of $(DAN)_2CH(OH)$ and $328.4 + 5.0°$ (PL = 15.8%) for the dicyclopropylcarbinol DAN-$C(C_3H_5)_2(OH)$. The virtual identity of the data of the two DAN groups in $(DAN)_2CH(OH)$ deserves attention, because only one of them qualifies for a N···H–O hydrogen bond [1]. This feature may indicate that hydrogen bonds, though *bonds*, do not affect the N-planarization (*vide infra*). The no-bond angles $C_{peri}\cdots$N–C add to sums of *ca.* 320° so that accidentally the sum of all six angles differs from 656.8° only by a few degrees (subsets B and sum of all angles: (S)-DAN-CH(Ph)(OH) $328.4 - 11.4°$, $656.8 - 2.9°$; (R)-DAN-CH(Ph)(OH) $328.4 - 15.1°$, $656.8 - 3.3°$; $(DAN)_2CH(OH)$ $328.4 - 8.2°/-10.0°$, $656.8 - 2.2°/-3.5°$; DAN-$C(C_3H_5)_2(OH)$ $328.4 - 8.1°$, $656.8 - 3.1°$).

In a compound in which two DAN groups are attached to the C(sp^3) atoms of a 1,3-disilacyclobutane ring [39] (Table 1, entry 7), the N···C(sp^3) distance is 298.5/297.5 pm [40]. Large splay angles ($+8.1°/+10.2°$) and considerable deviations of the C_{10} skeleton from planarity reflect strong steric repulsion. Both N atoms are strongly planarized (subsets A: $328.4 + 11.0°/+10.6°$; PL = 34.8/33.5%; subsets B: $328.4 - 14.7°$; all angles: $656.8 - 3.7/-4.1°$).

In a silane DAN-$SiMe_2R$ in which a C(1)-bound 1,4-dihydro-DAN group is part of the substituent R [41] (Table 1, entry 43), the Me_2N group of the latter is planarized to the extent of PL = 36.7%. For the N···Si segment, $d(N\cdots Si) = 304.6$ pm and the splay angle of $+8.7°$ indicate the absence of N→Si bonding; planarization amounts to PL = 22.2%. Similarly, in 8-$(PhCH_2)_2N$-$C_{10}H_6Br$ [4] (Table 1, entry 8),

$d(\mathrm{N}\cdots\mathrm{Br}) = 299.1$ pm and the splay angle $+9.4°$ are evidence of steric repulsion. Subset A amounts to $328.4 + 14.9°$ (PL = 47.2%), the three Br···N–C angles (subset B) to 309.5° and the sum of all six angles to $656.8 - 4.0°$.

DAN-NR$_2$ compounds

The *proton sponges* DAN-NR$_2$ represent another class of compounds with no *peri* bond. Consistently, $d(\mathrm{N}\cdots\mathrm{N})$ exceeds PD considerably, and the splay angle of the N–C(1/8) bonds is throughout positive. A selection of published data (15 compounds; Table 1, entries 9 – 25) reveals that the degree of planarization is always high (between PL = 39.6% in 1,8-$(Me_2N)_2$-4,5-$(MeO)_2C_{10}H_4$ and complete planarity in 1,8-$(Me_2N)_2$-2,7-$I_2C_{10}H_4$); only in 1,8-$(Me_2N)_2$-2-$((HO)Ph_2C)C_{10}H_5$, the Me_2N group on the less hindered side is less planarized (PL = 23.1%), while planarization at the N atom adjacent to the carbinol substituent falls into the general range (PL = 69.6%). An equally high degree of planarization is also shown by both N atoms of 1,8-$(Me_2N)_2$-2,7-$((HO)Ph_2C)_2C_{10}H_4$ (PL = 68.7% (N(1))/ 70.3% (N(8))). The lone pair of N(1) adopts a synperiplanar, that of N(8) an antiperiplanar conformation with respect to the C(1)···C(8) connecting line, so that – if any – only the latter qualifies for a hydrogen bond N···H–O. Again, no impact of hydrogen bonds upon PL is evident. The sums of the no-bond N···N–C angles (subset B) range from 238.5° to 318.3°, so that the sum of all six angles falls considerably short of 656.8° in spite of the strong planarization.

Protonated proton sponges (Table 1, entries 27 – 29) permit to study the impact of hydrogen bonds. Distances $d(\mathrm{N}\cdots\mathrm{N})$ exceeding PD only slightly and small splay angles indicate that their bonding energy is strong enough to counterbalance the FSR. However, in DAN-N^+HMe_2, the C–N–C angles (subset A) add to $328.4 + 7.4°/+6.4°$ (PL = 23.4/20.3%). The same degree of planarization is exhibited by DAN-OH [19] (Table 1, entry 26, $328.4 + 7.2°$; PL = 22.8%). As in the free base, 2,7-substitution of DAN-N^+HMe_2 widens the angles of subset A considerably and raises PL to *ca*. 45% (Table 1, entries 28, 29). The angles N···N–C (subset B) add to more than 310° so that the sum of all six angles is smaller than 656.8° only by a few degrees.

In conclusion, the planarization at N in N···H–N^+/O species, though somewhat smaller than in the corresponding free bases, remains considerable (PL > 20%): Though hydrogen bonds, too, are strongly attractive interactions, there remains a gap of Δ(PL) = *ca*. 15% which separates the realm of covalent *peri* bonding from that of hydrogen bonds.

DAN-C compounds with alleged weak N→C interactions

Schweizer *et al*. [42] and Clayden *et al*. [43] studied potential N→C interactions in DAN-C(=O)R compounds (R = Me, OH, OMe, NR'$_2$). Deviations of the –C(=O)R substituent from planarity and the *windshield wiper phenomenon* [2, 5] of the bay angles of the C_{10} skeleton induced Schweizer *et al*. [42] to regard the structures as frozen early stages on the reaction coordinate of nucleophilic addition of the amine to the carbonyl function. Several objections may be raised. The *windshield wiper phenomenon* is an artefact caused by the neglect of the central bay angle (C(1)–C(9)–C(8)) of the naphthalene skeleton [5]; in fact, both the splay angle and $d(\mathrm{N}\cdots\mathrm{C(=O)})$ provide unambiguous evidence of *peri* repulsion (Table 1, entries 30 – 34). In case of an attractive N→C(=O) interaction, both features should depend on the donor capacity of one *peri* substituent and the acceptor capacity of the other. This is not the case: Though MeO and HO exert a much smaller σ-donor effect than Me_2N, the degree of pyramidalization at C_{peri} and the splay angle are not reduced in the corresponding 8-MeO-/HO-$C_{10}H_6$-C(=O)R compounds [5]. Though the formal carbonyl C atom in amides is virtually devoid of electrophilic properties, N,N-dialkylamides DAN-C(=O)NR_2, R = Me, *i*Pr, and even 8-MeO-/HO-$C_{10}H_6$-C(=O)N*i*Pr_2 exhibit the same features. In view of the profoundly different electronic effects and the similar steric situation, it is appealing to assume that such uniform behaviour is a steric phenomenon rather than evidence of incipient N→C(=O) interactions. In fact, PL = 26.0 (R = N*i*Pr_2), 30.1 (NMe_2), 31.3 (Me, OMe) and 35.4% (OH) for DAN-C(=O)R is not indicative of covalent N→C(=O) bonding. In compliance with this result, planarization at the C(=O) atom amounts to PL = 95.9 – 98.7%, and at the amide N atom of DAN-C(=O)NR_2 to PL = 98.4% (R = Me) and 100% (R = *i*Pr). The amide group is thus almost perfectly planar and therefore unaffected by the Me_2N group. We conclude that in all cases, the *peri* bond order between N and C(=O) is not significantly different from zero and that the molecules are best represented by their conventional formulae.

DAN-Al/Ga/In compounds

In 1-(Me_3Al←$N(Me_2)$)$C_{10}H_7$ [44] (Table 1, entry 35), the sum of the C–N–C angles (subset A) amounts to $328.4 - 2.9°$: The NC_3 pyramid is even steeper than tetrahedral. Due to a moderate increase of the C–N–Al angles (subset B, $328.4 + 2.4°$), the sum of all six angles falls short of 656.8° by only 0.5°. Molecules in which Al occupies the second *peri* position (1-azonia-2-aluminata-acenaphthenes, Me_2N-$C_{10}H_6$-AlR_2) exhibit the same features (Table 1, entries 36 – 39, d(N–Al) < 212 pm, splay angles −14 to −16°, subset A/B: $328.4 + 1.1°/-1.2°$ (R = H) [45], $328.4 + 0.1°/\pm 0.0°$ (R = Me) [46], $328.4 + 1.1°/-1.1°$ (R = Et) [44], $328.4 + 0.4°/-0.6°$ (R = Cl) [45]), as do 2,2-dichloro-1,1-dimethyl-1-azonia-2-gallata-acenaphthene (Table 1, entry 40, subset A/B: $328.4 + 0.1°/-0.3°$ [45]) and – with slightly reduced precision – the corresponding indium compound (Table 1, entry 41, subset A/B: $328.4 + 2.2°/-2.1°$ [45]): In every respect, the N→Al/Ga/In bond conforms with astounding precision with the properties of a covalent two-electron bond, in no way different from related aliphatic or even acyclic systems, such as 1,1,2,2-tetramethyl- and 1,1-dimethyl-2,2-pentamethylen-1-azonia-2-aluminata-cyclopentane [46] (Table 2, entries 78, 79, subset A: $328.4 - 0.1°/-1.3°$, subset B: $328.4 - 0.1°/+1.1°$), the 2-borata analog of the latter [46] (Table 2, entry 80, 2 independent molecules; subset A: $328.4 - 0.3°/-0.8°$, subset B: $328.4 + 0.1°/+0.5°$), 2,2-dichloro-1,1,5-trimethyl-1-azonia-2-gallata-3,4-benzo-cyclopentane [46] (Table 2, entry 83, subset A/B: $328.4 + 1.4°/-1.7°$), Me_3N→GaH_3 (a Me_4N^+ analog in which one of the methyl carbon atoms is replaced by Ga) (Table 2, entry 81, sum of the three smallest/largest angles, $328.4 - 1.1°$ (C–N–C, subset A) and $328.4 + 1.0°$ (Ga–N–C, subset B)) [47], and quinuclidineGaH_3 (Table 2, entry 82; subset A/B: $328.4 - 3.7°/+3.6°$) [48]. No special properties of *dative bonds* are apparent, so that the molecules are best described by their conventional formulae (which place a positive charge on the N atom and a negative charge on the Al/Ga/In atom [49]) and a special symbol, →, for their bond is dispensable or even misleading.

"N→Si-stabilized silylenium cations"

Brelière *et al*. [50] prepared the salt 2 $(DAN)_2SiH^+$ $I_8{}^{2-}$ the cation of which was described as a species in which a Si(sp^2) (silylenium [51]) atom is stabilized by two intramolecular N→Si coordinations (Table 1, entry 42). d(N→Si) = 206.2/208.6 pm is *ca*. 6 pm longer than the axial Si–N bond in a recently synthesized BrN_2O_2*Si* heterocycle with TBP geometry [52]); the coordination around Si is distorted TBP: N–Si–N $180 - 12.2°$ (a/a); sum of e/e angles $360 - 1.8°$). Within the limits of the esd's, the sum of the a/e angles, $540 + 0.8°$, is perfect. The splay angles of the C(1/8)–Si/N bonds are strongly negative (−23.0/−19.5°). In compliance with these features, the six angles at each N atom add to perfect tetrahedrality ($656.8 - 0.5°/-0.8°$). The subsets A, $328.4 + 1.2°/+1.2°$, correspond to a formal PL = 3.8% which is still within the limits set by the R_4N^+ salts (*vide supra*). The cation can, therefore, be adequately classified as a 1,3-azonia-2-silata system (N^+–Si^-–N^+) with hypercoordinate Si and two axial covalent Si–N bonds.

For an assessment of PL = *ca*. 4%, comparison with an analogous bis(2-dimethylaminomethylphenyl) compound is worthwhile. Whether in arylsilicon compounds containing two *ortho*-CH_2NMe_2 groups one or both N atoms coordinate with the Si atom, depends subtly on the conditions [53]. In [(2-$Me_2NCH_2C_6H_4)_2SiH]^+$ $CF_3SO_3{}^-$ [54] (Table 2, entry 84), d(N–Si) = 205.2 /207.2 pm compares well with d(N–Si) = 206 to 208 pm in $(DAN)_2SiH^+$. Both Me_2N groups coordinate to the Si atom which, consequently, is not tetrahedral, but again the centre of a TBP. However, the trigonal pyramid of the subset A angles is slightly *steeper* than tetrahedral (328.4 – 0.7°/–1.3°); the subsets B (328.4 + 0.4/+0.6°) bring the sum of the six angles to virtually perfect tetrahedrality (656.8 – 0.3°/–0.7°): Again, *both* N atoms are engaged in R_3N^+–Si^-–N^+R_3 (or R_3N→Si←NR_3) covalent bonds, and the Si atom is hypercoordinate. The similarity of the pertinent data with those of the $(DAN)_2Si^+$ cation permits to conclude that this is the case in both salts.

DAN-Si=C and 2-Me_2NCH_2-C_6H_4-Si=C compounds

Oehme *et al*. prepared and investigated a series of compounds which were represented by an arylsilaethene formula [55 – 60]. When aryl was DAN or 2-$Me_2NCH_2C_6H_4$, the compounds exhibited an extraordinary stability and N···Si distances of *ca*. 200 – 207 pm; these features were ascribed to N→Si interaction; the compounds were called "intramolecularly amine-stabilized silenes" [56] and described by formulae which contain both a Si=C double bond and a Me_2N→Si dative bond. The meaning of both sym-

bols remains somewhat vague: Including the N atom, the Si atom has four nearest neighbours and is therefore tetra*coordinate* [55, 56]. On the other hand, if the dative arrow represents a dative covalent bond, the Si atom would be hyper*valent*; the Si=C bond would not be the Si analog of a C=C(p-p)$_\pi$ bond, but a Si=C(d-p)$_\pi$ bond or some more up-to-date type of hypervalent "double bond". A Si=C(p-p)$_\pi$ bond suggests a planar arrangement both for the Si and the C atom. Within the realm of the octet rule, formation of a N^+–Si bond would require the withdrawal of π-electrons from the Si atom and cause tetrahedralization of the latter. In fact, it deviates considerably from planarity, but is far from perfect tetrahedrality either, whereas the C atom is indeed virtually planar [55, 56]. While consistently speaking of "silenes" and almost exclusively using the corresponding formula, Oehme *et al*. concluded that "the structural data… agree with our notion about the ylide-like nature of the two donor-stabilized silenes" [56] for which the pertinent formula (with the Me_2N^+–Si–C^- segment containing tetracovalent Si) was used, albeit in a bond/no bond resonance relation with the (dimethylamino)aryl-silaethene formula. The relative weight of the two resonance formulae was not assessed [61].

In "DAN-Si($SiMe_3$)=C($SiMe_3$)$_2$" [55] (Table 1, entry 44), d(N–Si) = 206.9 pm (shorter than PD by 44 pm) and a negative splay angle of $-14.9°$ are again evidence of strong attractive forces. Subset A amounts to $328.4 + 1.7°$, hence a formal planarization of PL = 5.4%. As in $(DAN)_2SiH^+$, the slight excess of the C–N–C angles is compensated by the Si–N–C angles (subset B: $328.4 - 1.8°$) so that all six angles make up a perfect tetrahedron ($\sum$(C–N–Si/C) $= 656.8 - 0.1°$). The steep trigonal pyramid of the Si–N–C angles contrasts sharply with the nearly planar geometry around the N atom in amino-silanes [34, 62 – 65].

Two "2-Me_2NCH_2-C_6H_3R-Si($SiMe_3$)=C($SiMe_3$)$_2$" compounds (R = H, CH_2NMe_2) (Table 2, entries 86, 87) perform even better. Subset A amounts to $328.4 + 0.4°$ and $328.4 - 0.5°$, respectively [66]. We conclude that in all cases a full covalent bond N^+–Si has formed and that the DAN compound is satisfactorily described as C-deprotonated (hence zwitterionic) 2-(bis(trimethylsilyl)methyl)-1,1-dimethyl-2-trimethylsilyl-1-azonia-2-sila-acenaphthene. Considerable C-H acidity of the conjugate acid would be anticipated due to three Si atoms in α-positions (*cf.* the Peterson olefination [67]): Oehme's ylidic formula is an adequate representation of the molecule while the silene formula is misleading. The ylidic formula explains the entirely different chemical properties of the stable DAN-Si compounds and the corresponding 8-MeO-$C_{10}H_6$-Si compounds which are indeed aryl-substituted silenes because of the poor σ-donicity of MeO and hence unstable. The differences of chemical behaviour contrast with the uniformity shown by the 8-Me_2N-/MeO-$C_{10}H_6$-CO-R compounds [42, 43] in which N/O→C interactions play no significant role [5] (*vide supra*). The length of the Si–C bond, 175 – 176 pm, and the planarity at the ylidic C atom have their counterparts in phosphonium ylids where the ylidic C atom likewise tends to be planar and the P^+–C^- bond is shorter than other P^+–C single bonds [68]. The nearly planar geometry around the tricoordinate N atom of amino-silanes (the N-analogs of Si-ylids) [34, 62 – 65] is another analogy. The almost identical N$\cdots$Si distances in the DAN- and the 2-Me_2NCH_2-C_6H_3R- "silylenium" cations and "silenes" suggests that *ca*. 200 – 208 pm is the typical length of N^+–Si bonds and that the GPF of the DAN group is insufficient to enforce their stretching. The same length has been found in zwitterionic 1-(R_2N)$Hal_{3-n}Me_n$Si-substituted quinolinium structures ($n = 1, 2$, Hal = Cl) [63], hence in molecules which likewise contain one or two Si–C bonds, while analogous structures without Si–C bonds exhibit slightly shorter N^+–Si distances ($n = 0$, Hal = F, Cl: 197 – 198 pm [62, 64, 65]), in a compound with three Si–C bonds ($n = 3$; d(N$\cdots$Si) = 268.9 pm [34] as in silanes DAN-SiR_3) no N^+–Si bond is formed at all.

DAN-P/As/Sb compounds with d(N$\cdots$P/As/Sb) > PD and positive splay angles

All DAN-P compounds with d(N$\cdots$P) > PD and positive splay angles invariably feature substantial planarization at the N atom (Table 1, entries 45 – 50, 53 – 59). In most cases, PL of subset A is between *ca*. 20 and 37% with a minimum of 11% [69] (entry 54). Again accidentally, the P$\cdots$N–C angles (subset B) amount to *ca*. 320° so that the sum of all six angles deviates only little from 656.8°. The compounds include a DAN-phosphorane with five P–C bonds [70] (entry 49, PL = 12.7%) and a DAN-phosphonate [71] (entry 50) in which the three O atoms attached to the P atom ought to improve the prerequisites for N→P bonding. Nevertheless, d(N$\cdots$P) = 286.9 pm, the splay angle (+8.6°) and PL = 25.0% exclude a N→P bond. In

$(DAN)_3As$ [72] (entry 51), both the low electronegativity of As and the increased length of the As–C(1) bond render N→As bonds unfavourable; indeed, all criteria indicate the absence of such interaction. Not surprisingly, $(4\text{-Me-}C_6H_4)_2Sb$-DAN [29] (entry 52) shows essentially the same behaviour.

DAN-X compounds with $d(N\cdots X) \gg \sum r_{cov}[N,X]$, but $\ll PD$

In the pyrocatechol derivative DAN-$P(O_2C_6H_4)_2$ (Table 1, entry 60) with hexacoordinate P (including N→P coordination) [3], d(N–P) = 213.2 pm is 37 pm shorter than PD, but 33 pm (18%) longer than the sum of the single bond covalent radii, $\sum r_{cov}$[N, P] = 180 pm [73]. The crucial C–N–C angles (subset A) amount to only $328.4 - 1.9°$ (-6.0%) and thereby confirm the earlier conclusion that a full covalent bond (albeit dative, N→P, and hypercoordinate) exists between N and P [3]. An excess of 1.9° in subset B (the C–N–P angles) brings the total to perfect tetrahedrality (656.8°). The exalted length of the N^+–P^- bond can be accounted for by the assumption that hypercoordinate N→P bonds are either longer than non-hypercoordinate N–P bonds or so much weaker that the FSR and GPF are strong enough to enforce unusual bond stretching. Notwithstanding unsettled problems in the rationalization of hypercoordinate bonds [74], the assumption is legitimate in view of an entirely different orbital situation at the P atom. The same phenomenon arises for hypercoordinate C–P bonds, albeit to a lesser degree (*e. g.*, in Ph_5P, $d(C_{apical}\text{–}P)$ = 198.7 pm [75], the biphenylylene parts of Ar-$P(C_{12}H_8)_2$, d(C–P) = 191.0–193.6 pm [70, 76]), a 6-carbaphosphatrane, d(C–P) = 193.4 pm [77], and the tris(2,2'-biphenylylene)phosphate $t\text{Bu}_4P^+$ $(C_{12}H_8)_3P^-$, d(C–P) = 193.6 pm [78], *ca.* 7–11% longer than $d(\text{C–P})[Ph_4P^+]$ = 178.9 pm [79]). It emerges that the N^+–P^- bond is weaker than its C–P analog. On the other hand, its stretchability is insufficient to permit a N···P distance longer than PD.

Several cases in which d(N···X) even exceeds d(N–P) in DAN-$P(O_2C_6H_4)_2$ deserve special attention. In the 1,3-dioxa-2-sila-cyclopentane derivative DAN-Si(H)$[O_2(CMe_2)_2]$ [26] (Table 1, entry 73), d(N···Si) = 233.9 pm and the splay angle, −7.9°, still indicate substantial attractive forces, but d(N···Si) is 20 pm longer than d(N···P) in DAN-$P(O_2C_6H_4)_2$ and exceeds $\sum r_{cov}$[N, Si] = 187 pm [73] by 25%. A moderate but considerable planarization at N (subset A: $328.4 + 3.3°$ (PL = 10.4%), subset B: $328.4 - 2.3°$, six angles: $656.8 + 1.0°$) raises doubts whether the attractive forces are of covalent nature. The geometry around the Si atom can be described as distorted TBP, but the Si atom is significantly displaced out of the equatorial plane towards the center of a O_2CH tetrahedron: The six bond angles O/C–Si–O/C/H add to $656.8 - 6.5°$ [80]. In terms of TBP, the a/a angle, N–Si–O^a, is $180 - 4.8°$. The sum of all six a/e angles, $540 + 0.6°$, complies well, but all O^a–Si–O^e/C/H angles are considerably larger than 90° (sum: $270 + 27.4°$) and all N^a–Si–O^e/C/H angles considerably more acute (sum: $270 - 26.8°$). Likewise, the sum of the three e/e angles, $360 - 7.1°$, is evidence of pyramidalization. These features indicate that the Si atom resides almost half way between the centres of the O^e/C/H triangular plane and a O^a/O^e/C/H tetrahedron (sum of the O^a–Si–O^e/C/H angles: $270 + 27.4°$ and $328.4 - 31.0°$, respectively). It emerges that the N atom is not fully coordinated, a conclusion with which the long N···Si distance and the comparatively small, but substantial PL are in full accord.

Almost the same N···Si distance (d(N···Si) = 228.7/231.8 pm in two independent molecules) and slightly smaller negative splay angles (−7.0/−6.1°) have been found in DAN-SiF_3 [23] (Table 1, entry 61). d(N···Si) = 231.8 pm exceeds $\sum r_{cov}$[N, Si] = 187 pm [73] by 24% and is even much longer than the N^+–Si bonds in the "donor-stabilized silylenium cations and silenes". At first sight, the geometry at the Si atom seems to be neatly TBP and therefore indicative of a N→Si bond: The a/a angle, N^a–Si–F^a, is $180 - 0.8°$. Of the a/e angles, N^a–Si–C(1), 80.5°, should indeed be acute, and Si–N–C(8), 104.9°, should be larger than 90° because of the bond lengths, $d(\text{N–C(8)}) < d(\text{Si–C(1)})$ [3]. The sum of all six a/e angles, 540.1°, agrees perfectly with an ideal TBP (540.0°). However, again the sum of the three e/e angles, $360 - 5.2°$, is evidence of significant pyramidalization at Si. This is corroborated by the a/e angles F^a–Si–F^e/C which are all larger than 90° (sum: $270 + 22.6°$), and the a/e angles N^a–Si–F^e/C which are all more acute (sum: $270 - 29.9°$). The Si atom is, therefore, displaced by almost 40% from the equatorial plane towards the centre of a F_3C tetrahedron. On the other hand, the geometry around Si cannot satisfactorily be described as tetrahedral either (sum of all six F–Si–F/C angles only $656.8 - 9.4°$). In this case, the geometry at the N atom resolves the ambiguity in favour of a full covalent bond: The C–N–C angles (subset A: 328.5°) as well as the C–N–Si angles

(subset B: 328.3°) and the total (656.8°) exhibit perfect behaviour. Obviously, the attractive forces suffice to resist stretching to d(N–Si) = PD or to the N···Si distances in other DAN-silanes under the impact of the GPF and the FSR.

In the anion DAN-SiF_4^- [24] (Table 1, entry 62), the geometry at the Si atom is octahedral: The 12 *cis* angles add to 1080 − 1.8°, while the three *trans* angles, 180 − 1.9°/−7.0°/−15.0°, deviate moderately from a linear arrangement. In view of N···Si distances of 194−200 pm in compounds with a $N_2O_2X_2$ (X = C, Cl, F) octahedral coordination around Si [81], d(N–Si) = 221.3 pm is intriguingly long. However, the C–N–C angles (subset A: 328.4 − 0.9°) as well as the C–N–Si angles (subset B: 328.4 + 0.9°) exhibit almost perfect tetrahedrality. Again as anticipated, C(8)–N–Si, 107.7°, is larger, C(1)–Si–N, 81.1°, is more acute than 90°.

Interestingly, almost the same N···Si distance as in DAN-Si(H)[$O_2(CMe_2)_2$] has been found in (2-Me_2NCH_2-C_6H_4)-SiF_2Me (Table 2, entry 85) where free rotation around the C(sp^3)–C(sp^2) bond would permit the N atom to go to $\sum r_{vdW}$ distance (d(N···Si) = 234.6 pm [82], 25.5% longer than $\sum r_{cov}$[N, Si] = 187 pm, but 32% shorter than $\sum r_{vdW}$[N, Si] = 345 pm [40]). The C–N–C angles add to 328.4 − 1.6°, hence again form a trigonal pyramid even slightly steeper than tetrahedral. At the Si atom, a TBP geometry is indicated by the behaviour of the a/e angles (sum: 540 − 0.2°); the a/a angle, 180 − 6.5°, complies less satisfactorily. The e/e angles (sum: 360 − 15.3°) indicate considerable pyramidalization [82]. The sums of the a/e angles F^a–Si–F^e/C, 270 + 22.8°, and of the N^a–Si–F^e/C angles, 270 − 23.0°, show that the Si atom is displaced out of the equatorial plane towards the apical F atom to about the same extent as in DAN-SiF_3. Unlike in DAN-SiF_3, a N^+–Si^- bond would not be subject to the GPF; the similarity of d(N···Si) may therefore once more indicate that its great length is not due to an exalted stretchability (*vide supra*).

In the pyrocatechol derivative Ph(2-Me_2NCH_2-C_6H_4)Si($O_2C_6H_4$) [83] (Table 2, entry 88), subset A amounts to 328.4 − 0.7°, subset B to 328.4 + 0.5° and the total to 656.8 − 0.2°. Though the individual angles around Si deviate considerably from ideal TBP behaviour, their sums still permit to describe the geometry as TBP (6 · a/e : 540 + 2.9°, a/a : 180 − 13.9°). 3 · e/e : 360 − 2.5° and the sums of the O^a–Si–O^e/C (270 + 16.5°) and the N^a–Si–O^e/C angles (270 − 13.6°) indicate some pyramidalization [84] which, however, is smaller than in (2-Me_2NCH_2-C_6H_4)-SiF_2Me. Also in three pyrocatechol derivatives [(2-Me_2NCH_2-6-R-C_6H_3)-Si($O_2C_6H_4$)$_2$]$^-$ (R = H [85] /Me_2NCH_2 [35a] /$Me_2HN^+CH_2$ [86]) (Table 2, entries 89 − 91), the trigonal pyramids of the C–N–C angles are slightly steeper than tetrahedral (subsets A: 328.4 − 3.2°/−1.8°/−2.4°) while the sums of all C–N–C/Si angles (always 656.8 − 0.2°) are perfectly tetrahedral due to a slight increase of the subset B sums (328.4 + 3.0°/+1.6°/+2.2°). The 2,6-bis(dimethylaminomethyl) compound is of particular interest because it contains a coordinated and an uncoordinated Me_2N group side by side. The N atom of the latter is partially planarized: subset A 328.4 + 3.2° (PL = 10.1%). In conformity with other benzyldimethylamines, the planarization is less pronounced than in DAN-X compounds (*vide supra*). Nevertheless, the result is unambiguous, because the H_2C–N^+Me_2 pyramid of the coordinated N atom is steeper than tetrahedral. If for the degree of planarization, instead of 328.4°, the subset A value of the H_2C–N^+Me_2–Si segment is used as an internal reference, PL = 15.0% is obtained. In all three compounds, the geometry around Si is an octahedron whose quality resembles that of DAN-SiF_4^-: sums of 12 *cis* angles 1080 + 0.5°/+0.1°/+0.3°, *trans* angles 180 − 4.8°/−7.3°/−12.7°, 180 − 5.7°/−9.6°/−15.1°, 180 − 4.1/−5.4°/−11.3°.

Essentially the same behaviour is shown by (2-Me_2NCH_2-C_6H_4)$_2$$SiCl_2$ [35b, c] (Table 2, entry 92). Only one N coordinates (d(N^1···Si) = 229.1 pm; d(N^2···Si) = 449.3 pm; N^1: subset A steeper than tetrahedral (328.4 − 1.5°), subset B 328.4 + 1.1°, all six angles 656.8 − 0.4°; N^2: subset A 328.4 + 2.9°, PL = 9.2% (based on 328.4°), 13.3% (based on subset A of N^1 as internal reference)). The geometry around the Si atom can be described as a slightly distorted TBP (sum of six a/e angles 540 + 0.2°, a/a angle (N^1–Si–Cl) 180 − 2.7°). Though d(N···Si) is 12.8 pm longer than in Ph(2-Me_2NCH_2-C_6H_4)Si($O_2C_6H_4$), pyramidalization at the Si atom is about the same (sum of the three e/e angles: 360 − 3.1°, of the a/e angles: Cl^a–Si–Cl^e/C: 270 + 17.1°, N^a–Si–Cl^e/C: 270 − 16.8°).

Interestingly, the change from the aryl to the corresponding ferrocenyl compound suffices to prevent N→Si coordination: In the bis(ferrocenyl) silanes [C_5H_5→Fe←(2-Me_2NCH_2-C_5H_3)]$_2$$SiR_2$ (R = Cl, Me [35e], OH [35d]) (Table 2, entries 103 − 105) the distances (d(N···Si) = 354.7/403.2

(R = Cl), 376.8/415.9 (Me), 351.4/364.6 (OH), all $> \sum r_{vdW}[N, Si]$) do not indicate a covalent interaction [35e]. The subset A sums (Cl: $328.4 + 5.1°/+2.9°$, Me: $328.4 + 5.1°/+3.9°$, OH: $328.4 + 3.5°/+3.1°$) correspond to PL = 16.1/9.2%, 16.1/12.3% and 11.1/9.8%, respectively. The sums of all six C–N–C/Si angles range from $656.8 - 15.8°$ to $656.8 - 5.1°$, because the no-bond angles C–N–Si do not compensate the increase caused by the planarization (subsets B from 308.7 to 318.2°). In compliance with this result, the tetrahedrality around the Si atom is perfect (sum of six C/O–Si–C/O angles: R = Cl: $656.8 - 0.3°$, Me: $+0.1°$ [35e], OH: $\pm 0.0°$ [35d]). The reason for the different behaviour may be that in the planar, symmetrical pentagon the splay angle of "*ortho*" bonds is 20% larger than in the planar hexagon and therefore less favourable for an approach of the N atom to the Si atom.

For $(DAN)_2AlEt$ [44] (Table 1, entry 63), the octet rule would permit only one DAN group to form a N→Al bond. However, since P and Si can be hypercoordinate in DAN-P/Si compounds, hypercoordinate Al in DAN-Al molecules must be considered. Indeed, $(DAN)_2AlEt$ contains two almost equal DAN groups whose N···Al distances exceed those in DAN-AlR_2 (R = alkyl, Cl) by *ca*. 20 – 25 pm, but are still much shorter than PD = 251.8 pm [87], and the splay angles of which are negative. The C–N–C angles as well as the C–N–Al angles differ little from ideal behaviour (subset A: $328.4 - 0.2°/+0.7°$; subset B: $-0.5°/-1.0°$; six angles: $656.8 - 0.7°/-0.3°$).

The conclusion that both N atoms are involved in N→Al bonds which behave as normal covalent bonds in spite of their length, is corroborated by the geometry around the Al atom which can be very well described as a TBP with the N atoms in the apical positions (angles N^1–Al–N^2: $180 - 5.4°$ (a/a); C–Al–C: 131.37/109.58/119.05°, sum 360.0° (e/e); N^1–Al–C: 94.28/79.79/97.81°, sum $270 + 1.9°$ (a/e); N^2–Al–C: 90.73/78.61/98.35°, sum $270 - 2.3°$ (a/e); N–Al–C(1): 79.79/78.61° more acute, Al–N–C(8): 104.02/100.50° larger than 90° because of d(N–C(8)) $<$ d(Al–C(1))).

Cases of "secondary bonding"

While so far a consistent picture emerges, two DAN-Se-Hal compounds (Hal = Cl, I) [88] do not comply (Table 1, entries 67, 68). The N···Se distances are longer than $\sum r_{cov}[N, Se]$ = 187 pm [73] by 16/20%, but again much shorter than PD, and the splay angles are negative. While attractive forces must be operative, PL = 20.3/21.8% of the C–N–C angles is within the range typical for uncoordinated N. The C–N···Se angles amount to 321.8°/321.3° (subset B) so that all six C–N–C/Se angles comply with a perfect tetrahedron (sum $656.8 - 0.2°$). The same behaviour is exhibited by a tellurium halide, DAN-Te-Br [89] (Table 1, entry 69, d(N···Te) longer than $\sum r_{cov}[N, Te]$ = 207 pm [73] by 16%, splay angle $-6.1°$, PL = 13.0%, subset B: 324.2°, all six angles $656.8 - 0.1°$). In DAN-Te-S-CS-NEt_2 [88] (Table 1, entry 70), the splay angle, $-3.3°$, and d(N···Te) = 250.5 pm, slightly shorter than PD = 256 pm, indicate attractive interactions, but d(N···Te) is longer than $\sum r_{cov}[N, Te]$ by 21%. The sum of all six angles C–N–C/Te is $656.8 - 0.2°$, but the N atom is substantially planarized (PL = 17.4%). Interestingly, replacement of the DAN group by 2-$Me_2NCH_2C_6H_4$ has a very small effect: In 2-$Me_2NCH_2C_6H_4$-Te-I [90] (Table 2, entry 95), d(N···Te) is slightly shorter than in DAN-Te-Br; PL = 17.7% is the same as in DAN-Te-S-CS-NEt_2. On the other hand, replacement of the Hal or S atom at Te by C or Te causes a strong increase of d(N···Te) (Tables 1, 2, entries 71, 72, 96). In the DAN compounds [89], the increase is limited by the GPF (DAN-Te-Ph: d(N···Te) = 271.3 pm; (DAN-Te-)$_2$: d(N···Te) = 269.9/274.3 pm); the compounds exhibit all criteria of steric repulsion; as expected, planarization at N is substantial (PL = 29.4 and 26.9/27.8%, respectively). No longer restricted by GPF, the N···Te distances are much longer in $(2\text{-}Me_2NCH_2C_6H_4)_2Te$ (304.8 and 314.5 pm) [90], albeit still shorter than $\sum r_{vdw}[N, Te]$ = 355 pm by 11 and 14%; the planarization at N is in the same range as in DAN-Te-S-CS-NEt_2 (PL = 16.1/22.8%). The obvious conclusion is that in all cases except DAN-Te-Ph and (DAN-Te-)$_2$, attractive N···Se/Te interactions are operative which, however, are not of the N→Se/Te covalent bond type. Phenomenologically, these interactions comply with the definition of *secondary bonds* [91].

Related compounds of the $[2,6\text{-}(Me_2NCH_2)_2C_6H_3\text{-}X]^+$, X = S, Se, Te, type have also been investigated [92, 93] and the crystal structure of the sulfenium hexafluorophosphate determined [93] (Table 2, entry 94). The cation exhibits two equal N···S distances, d(N···S) = 206.3 pm (18.6% longer than $\sum r_{cov}[N, S]$ = 174 pm [73], but 38.4% shorter than $\sum r_{vdW}[N, S]$ = 335 pm [40]). Though all six angles around each N atom add to the sum of perfect tetrahedrality ($656.8 - 0.4°$), subset A ($328.4 + 7.1°$) indicates considerable planarization (PL = 22.5%) while subset B falls short of 328.4° by 7.5°: The struc-

ture can be well described as a Lewis base-stabilized sulfenium cation though (as in the DAN-Se-Hal compounds) the nature of the attractive force remains unknown and cannot therefore be adequately described as a dative bond. Attractive forces of non-covalent nature must also be operative in (2-Me_2NCH_2-C_6H_4)$_3$As and a number of antimony compounds 2-Me_2NCHR-C_6H_4-SbR'$_2$, R = H, Me, [35f, 72] (Table 2, entries 97 – 102) in which the N···As/Sb distances range from 280 to 304 pm, 33 to 59% longer than $\sum r_{cov}$ [N, As/Sb] = 191/211 pm [73], but 15 to 7% shorter than $\sum r_{vdW}$[N, As/Sb] = 325/330 pm [40], though a distance d(N···As/Sb) $\approx \sum r_{vdW}$ is not impeded by GPF. Planarization at N ranges from 10 to 31%, as is typical for non-coordinating Me_2N groups. These attractive forces of unidentified nature have been called *weak secondary interactions* [72].

Interestingly, the same peculiar features are also shown by a DAN-C compound. The alkenes DAN-CH=CR_2, R = COPh, CN [25] (Table 1, entries 65, 66), are carbon analogs of Oehme's "silenes". Donor action of Me_2N on the *peri*-C atom can be envisaged, because it would create zwitterionic species with a $N^+ - C_{peri}$ bond and the negative charge delocalized in the XC–C–CX (X = O, N) segments. However, in either case a strong planarization at N is incompatible with N→C bond formation (R = COPh/CN: subset A: 328.4 + 12.8°/+12.4°, PL = 40.5/39.1%; subset B: 312.3°/314.3°; all angles 656.8 – 3.3°/–1.7°). The C=C bonds retain their double bond character (R = COPh/CN: d(C=C) = 134.1/135.4 pm, $\sum r_{cov}$[C(sp^2), C(sp^2)] = 133 pm [94]). The conclusion is that N→C_{peri} bonding plays no role. For R = COPh, this is corroborated by d(N···C_{peri}) = 267.9 pm and the positive splay angle, +4.3°. In the malononitrile (R = CN), d(N···C_{peri}) = 241.3 pm, much too long for a covalent N–C bond ($\sum r_{cov}$[N, C] = 147.1 pm [73]), but shorter than PD by *ca.* 5 pm, and a significant negative splay angle (–3.5°) are evidence that the FSR and the GPF are overcompensated by an attractive force which, however, cannot be a covalent bond.

Borderline cases

In a few DAN-X compounds, d(N···X) is shorter than the SRF would permit, but not much different from or even slightly exceeding PD, and the splay angles of the C(1)–X and the C(8)–N bonds are close to zero or even slightly positive. Both features indicate that some force must be operative which counteracts the SRF, but which hardly qualifies for a covalent bond. *E. g.*, in the pyrocatechol compound (DAN)$_2$Si($O_2C_6H_4$) [27] (Table 1, entry 74), one N···Si distance may be ascribed solely to *peri*-repulsion (d(N···Si) = 264 pm, splay angle +3.3°), but the other one exceeds PD by only 5 pm (d(N···Si) = 256 pm, splay angle +0.7°). The longer distance corresponds with a subset A angle sum of 328.4 + 3.3° (PL = 10.4%), hence a degree of planarization outside the range of covalent interaction. Subset B amounts to 328.4 – 3.7° so that the sum of the six angles is close to tetrahedrality (656.8 – 0.4°).

For the second DAN group, the respective figures are subset A 328.4 + 1.3°, PL = 4.1%, subset B 328.4 – 1.5°, six angles 656.8 – 0.2°. A covalent interaction cannot, therefore, be excluded, though d(N···Si) and PL may likewise be conditioned by other factors. A different attractive force may be operative, but the presence of a second DAN group in the congested *peri* space may sterically prevent adequate planarization. The geometry around the Si atom does not permit a decision, as it can be described as severely distorted tetrahedral (only angles O/C–Si–C/O considered; sum 656.8 – 11.5°), equally distorted TBP (angles with the more distant N disregarded as no-bond angles; a/a: 180 – 5.3°, e/e: sum 360 – 9.0°, a/e: sum 540 – 2.3°) and much distorted octahedral (all angles with both N atoms included; 3 *trans* angles: 180 – 5.3°/ –3.6°/ –35.4, 12 *cis* angles: from 74.7 to 104.2°, sum 1080 +3.3°). A countercheck reveals the shortcomings of this geometric consideration: If the check for TBP geometry is applied to the more distant N atom and the N–Si–C/O angles of the closer N atom are disregarded, compliance with perfect TBP geometry should deteriorate. In fact, it does so only for the e/e angles (sum: 360 – 13.5°) while it improves for the a/a angle (180 – 3.6°) and the sum of the a/e angles (540 – 1.8°).

Spiniello and White investigated the disiloxane [Me_2(DAN)Si]$_2$O and its silacyclobutane analog [(CH_2)$_3$(DAN)Si]$_2$O [28] (Table 1, entries 75, 76). The tetramethyl compound exhibits all features of a sterically hindered DAN-silane with no N→Si interaction (d(N···Si) = 284.9/285.1 pm, splay angles +2.0/ + 3.2°, subset A angles: 328.4 + 4.5°/+6.1°, PL = 14.2/19.3%). In the silacyclobutane compound, d(N···Si) = 261.4/262.1 pm is much smaller, and the splay angles even slightly negative (–0.7°/–1.0°). Though no significantly different impact of Me_2 and (CH_2)$_3$ upon the acceptor quality of the Si atom would be anticipated, these features were ascribed to in-

creased Lewis acidity of the Si atoms [28], hence to N→Si interaction. This is ruled out by the planarization at the N atoms which even slightly exceeds that of the tetramethyl compound (subset A: $328.4 + 5.7°/+6.6°$, PL = 18.0/20.9%). It may be more appealing to rationalize the reduction of d(N···Si) and the splay angles as a steric phenomenon: Not surprisingly, the angles C(sp^3)–Si–C(sp^3), 112.5°/112.6° in the tetramethyl compound, are much more acute in the silacyclobutane analog (77.3°/77.8°). This permits the $C(1)_{DAN}$–Si–O angles to widen from 101.4°/101.1° to 110.8°/110.7° and thereby to attenuate the congestion in the *peri* space [95]. Though short, d(N···Si) = *ca.* 262 pm is still in the realm of repulsion, while deviations of the C_{10} skeleton from planarity would trigger a reduction of the splay angles [96].

$(4\text{-}MeC_6H_4)_2Sb$-DAN adds Cl_2 to give $(4\text{-}MeC_6H_4)_2Cl_2Sb$-DAN [29] (Table 1, entry 77). d(Sb–C(1)) shrinks by 2.6 pm while d(N–C(8)) expands by 5.8 pm so that PD decreases from 258.0 to 255.7 pm. Indeed, d(N···Sb) = 265.8 pm is only 10 pm longer, and the splay angle, +1.0°, is small. If a hypercoordinate N→Sb bond is assumed to exceed $\sum r_{cov}[N, Sb]$ to the same degree as the N→P bond in DAN-$P(O_2C_6H_4)_2$ does, *viz.* 18%, a length of 249 pm would be anticipated. Such a bond would be expected to meet only little resistance by the GPF and to require only the attractive force to overcome the SRF. A N→Sb bond, therefore, must be considered. The N–Sb–C/Cl angles would be bond angles, and the geometry around the Sb atom should be distorted-octahedral. Indeed, it can be described in that way: three *trans* angles (Cl–Sb–Cl, N–Sb–C(Ph^I), C(1)–Sb–C(Ph^{II}), $180 - 7.7°/-5.3°/-24.3°$), twelve *cis* angles, sum: $1080 - 2.6°$. However, the nearly linear alignment N–Sb–C(Ph^I) may likewise be a consequence of other geometric features [74]. In an idealized naphthalene DAN-SbX_4 (splay angle 0°) with d(Sb–C(1)), d(N–C(8)) as found, the no-bond angles Sb···N–C(8) and N···Sb–C(1) would be 105.7° and 74.3°, respectively; found 103.3° and 73.9°. A description as distorted TBP (hence omitting the N···Sb–C/Cl angles as no-bond angles) is equally feasible: a/a (Cl–Sb–Cl) $180 - 7.7°$, sum of six a/e angles $540 + 2.9°$, sum of three e/e angles $360 - 0.1°$. The geometry around the Sb atom thus fails to permit a decision. The sum of all six C–N–C/Sb angles, $656.8 - 0.1°$, is compatible with perfect tetrahedrality, but not decisive either. It is only the partial planarization expressed by the C–N–C angles (subset A: $328.4 + 3.5°$, PL = 11.1%) which makes a covalent N→Sb interaction unlikely and suggests that some other property [97] may be responsible for the comparatively small N···Sb distance.

Conclusions

The present survey leads to the following results:

1) Clear-cut cases of DAN-X_{peri} compounds with or without a N–X bond show that the absence or the presence of partial planarization at the N atom is a safe indicator to decide whether an attractive interaction of covalent bond type is operative or not.

2) "Dative" (or "coordinative") N→Al/Ga/In/Si/P *etc.* *peri* bonds have the properties of normal covalent bonds. Within the realm of the octet rule, they do not show an idiosyncratic behaviour such as greatly enhanced stretchability. Consequently, the use of a special symbol, →, is unwarranted. The arbitrary procedure to divide the electrons of such bonds equally among both atoms leads to formal charges which cannot express the real charge distribution because the differences of the electronegativities are not taken into account. Valence bond formulas, however, benefit from the use of the formal charges, because ambiguities are eliminated.

3) "N-donor-stabilized DAN-silenes" are in fact zwitterionic compounds with a N^+–Si covalent bond in which the Si atom obeys the octet rule. The respective valence bond formula is an adequate representation.

4) Besides P and Si, Al can be hypercoordinate. In hypercoordinate DAN-Al/Si/P compounds, the N^+–Al/Si/P bond is much longer than ordinary N–Al/Si/P single bonds. Covalent radii derived from the latter are not applicable.

5) Other types of attractive interactions, *e.g.* hydrogen bonds and attractive forces of unidentified nature found in DAN-Se/Te compounds and in DAN-$CH{=}C(CN)_2$, are capable of establishing foreshortened N···C/Se/Te distances. The non-covalent attractive force operative in DAN-$CH{=}C(CN)_2$ and DAN-Se-Hal is strong enough to overcompensate steric repulsion of the *peri* substituents and the geometry preserving forces of the C_{10} skeleton. Hence, from evidence for intersubstituent attractive interactions in *peri*-substituted naphthalenes, no conclusions can be drawn that such interaction is of *covalent* nature.

Acknowledgement

The author is indebted to Professor H. Homborg for his help in handling structural data.

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[13] According to A. Haaland (Angew. Chem. **101**, 1017 (1989), Angew. Chem., Int. Ed. Engl. **28**, 992 (1989)), a covalent bond is dative if the bond rupture energy of heterolytic bond breaking is lower that that of homolytic bond scission. The practical value of such discrimination is limited, as the actual type of bond breaking may be determined by extramolecular factors. *E. g.*, homolytic scission may occur in nonpolar solvents, whereas heterolytic scission may be favoured by polar solvents because the resulting ions are stabilized by solvation. The dichotomy of *dative* and "normal" covalent bonds may therefore be more a concept than reflect real properties; *e. g.*, it serves to conceal the close similarity between 2,3,4,5-tetramethyl-2,4-hexadiene and its 2,4-diazonia-3,5-diborata analog (K.-A. Østby, G. Gundersen, A. Haaland, H. Nöth, J. Chem. Soc., Dalton Trans. 2284 (2005)). – *Cf.* V. I. Minkin, Pure Appl. Chem. **71**, 1919 (1999).
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[15] *E. g.*, in a recent review the Al atom of aluminium β-

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[34] For d(N···X), *vide supra*. The tetrahedra and TBP's are always distorted, and it is a matter of taste whether an irregular arrangement of five points around a centre with one of them at a significantly larger distance is described as a distorted TBP or as a distorted tetrahedron with an extra neighbour (*cf*., *e. g*., G. Klebe, J. Organomet. Chem. **293**, 147 (1985)). A formula proposed to calculate degrees of TBP character from angles (deviations from 109.47° *vs*. 90° and 120° in TBP) (K. Tamao, T. Hayashi, Y. Ito, M. Shiro, Organometallics **11**, 2099 (1992)) is obviously inapplicable in DAN-X systems where various parameters enforce unnatural bond angles [5].

[35] *Cf*. *ortho*-X-C_6H_4-CH_2NMe_2 structures and analogous ferrocenes where large distances d(N···X) are evidence that there is no significant N→X coordination, *e. g*. a) F. Carré, C. Chuit, R. J. P. Corriu, A. Fanta, A. Mehdi, C. Reyé, Organometallics **14**, 194 (1995); b) R. Probst, C. Leis, S. Gamper, E. Herdtweck, C. Zybill, N. Auner, Angew. Chem. **103**, 1155 (1991), Angew. Chem. Int Ed. Engl. **30**, 1132 (1991); c) H. Handwerker, C. Leis, R. Probst, P. Bissinger, A. Grohmann, P. Kiprov, E. Herdtweck, J. Blümel, N. Auner, C. Zybill, Organometallics **12**, 2162 (1993); d) V. Lorenz, K. Jacob, C. Wagner, H. Görls, Z. Anorg. Allg. Chem. **628**, 2855 (2002);

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[36] In DAN-X compounds, X prevents coplanarity of the C_{10} system and the Me_2N group. In benzene derivatives R-$C_6H_4NMe_2$ where coplanarity and, hence, efficient N/Ar resonance is possible, planarization at N is strong (*e.g.* in 3-$O_2NC_6H_4NMe_2$, formal PL = 97.5%, quantitative within the esd's: Y. Delugeard, J. C. Messager, Acta Crystallogr. **B31**, 2809 (1975)). In the thiaazacrown ether 4-$Me_2NC_6H_4N[(CH_2)_3$-S-$(CH_2)_2]_2S$, PL is 60.2% at Me_2N and 62.2% at the heterocyclic N atom. Engagement of the lone pair of the latter in a coordinative N→Pt bond causes the C–N–C angles to shrink to $\sum$(C–N–C) = 328.4 – 3.2° while PL(Me_2N) increases to 85.8% (J. W. Sibert, P. B. Forshee, V. Lynch, Inorg. Chem. **44**, 8602 (2005)).

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[38] *Perfect* refers always to the sum of the angles; deviations of the individual angles from 109.47° are a matter of course. For small formal deviations from 328.4°/656.8°, the esd's of the individual angles should be taken into account.

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