

***peri*-Interactions in Naphthalenes, 7 [1].
A Hetera-naphthalene as a Model Compound for 8-Dimethylamino-naphth-1-yl Silicon and Phosphorus Compounds**

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peri-Interactions in Naphthalenes, Phosphorus Compounds

In a 4-isopropyl-1-oxa-3-oxonia-2-borata-naphthalene the isopropyl group exhibits the same conformational phenomena as the Me₂N group in 8-dimethylamino-naphth-1-yl-silanes and related phosphorus compounds. Since the details can be fully rationalized on the basis of the steric situation and electronic factors are excluded, the common features cannot serve to infer dative interaction from nitrogen to silicon / phosphorus resulting in hypercoordination of the third period element atoms in the reference compounds.

Introduction

Late 20th century research on organosilicon compounds led to the impression that hypercoordination at silicon plays a much greater role than previously recognized [2]. In the realm of structural chemistry, this assessment rests to a significant extent on investigations of 8-dimethylamino-naphth-1-yl (“DAN”) silanes. Such silanes and analogous DAN phosphorus compounds exhibit certain common features:

(a) The distance $d(\text{N}\cdots\text{Si/P})$ is significantly shorter than the sum of the respective van der Waals radii, $\Sigma r_{\text{vdW}}(\text{N}, \text{Si/P})$.

(b) The sum of the valence angles Si/P-C(1)-C(9), C(1)-C(9)-C(8) and N-C(8)-C(9) (the “bay angles”) exceeds 360°, *i. e.* the splay angle of the *peri* bonds Si/P-C(1) and N-C(8) is positive.

(c) The Me groups of the Me₂N substituent reside in the *anti* hemicircle with respect to the C(1)⋯C(8) connecting line.

From (a), it has been inferred that there is a “weak dative interaction”, an “intramolecular donor-acceptor interaction”, N→Si/P, between the substituents by virtue of which the Si/P atom becomes hypercoordinate [3 - 14]. This interpretation has been believed to be supported by (c): From the *anti* positions of the Me groups above and below the naphthalene plane it was concluded that the lone pair at nitrogen points towards the Si/P atom and

that this direction is indicative of its involvement in a bonding N→Si/P interaction.

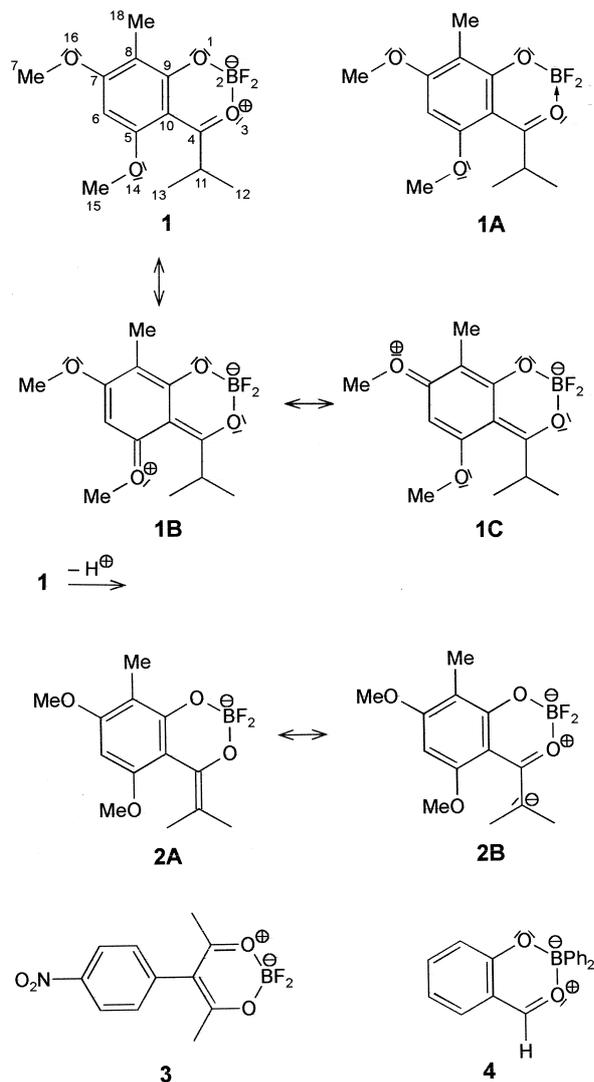
However, all these structural features can easily be rationalized without recourse to Si/P hypercoordination. $d(\text{N}\cdots\text{Si/P}) < \Sigma r_{\text{vdW}}(\text{N}, \text{Si/P})$ is a matter of course dictated by the geometry of the naphthalene system [1, 15 - 18]. The feature is shared by *all* 1,8-disubstituted naphthalenes C₁₀XY in which there is no bonding interaction between the substituents X and Y. In most DAN-Si/P compounds as well as in any other such compounds C₁₀XY, the intersubstituent distance exceeds the “natural” *peri* distance PD (as defined by the geometry of a perfect naphthalene, *ca.* 250 pm [1, 15 - 18]) as a consequence of steric hindrance which is also reflected by (b) (and more or less pronounced out-of-plane deformations [19]). Obviously, in the range $\text{PD} < d(\text{X}\cdots\text{Y})$ (*e. g.*, $d(\text{N}\cdots\text{Si/P}) < \Sigma r_{\text{vdW}}$), the intersubstituent distance is not a property from which information about bonding interactions can be obtained.

It remains to investigate in more detail the conformation of the N-bound methyl groups (c). Similar to $d(\text{N}\cdots\text{Si/P})$ and the splay angle, their *anti* position could be dictated by the steric situation in so far as the Me groups, more space-demanding and less amenable to deformation and compression than the lone pair, adopt positions in the less congested *anti* hemicircle and thus force the lone pair into

the less spacious *syn* hemicycle. Within the latter, the conformation having the lone pair eclipsed with the naphthalene plane would appear the most unfavourable one so that the interplay of the steric demands of the Me groups and the lone pair may be expected to result in a skew conformation in which the lone pair is in a *synperiplanar* (*sp*) position [20] though no longer in the C₁₀ plane, and the Me groups unsymmetrically distributed in the *anti* hemicycle. This is what actually has been found, *e. g.*, in DAN-phosphonium salts [1]. 1,8-Bis(dimethylamino)naphthalene (DAN-NMe₂) adopts a similar conformation in which the lone pairs reside in the *synclinal* (*sc*) sectors [21]. The greater deviation from being coplanar with the C₁₀ system can be rationalized as a consequence of electrostatic repulsion between the two lone pairs.

In order to further test this concept, it would be desirable to turn to a model compound C₁₀XY in which the steric situation is similar to that in the DAN-Si/P compounds but a bonding interaction between X and Y is precluded. The presence of Si or P could be conceded if the N-lone pair is removed, but is not mandatory. The lone pair should be replaced by a substituent smaller than Me. An isopropyl group instead of Me₂N would comply with the requirements. Since in the solid state, inversion at nitrogen in DAN compounds is “frozen”, it does not matter that in the Me₂(H)C group the tertiary carbon atom is configurationally stable and the nitrogen atom of Me₂N in principle is not. The target compound would therefore be a *peri*-disubstituted naphthalene C₁₀XY in which X is isopropyl and Y any substituent.

Unfortunately, 8-substituted 1-isopropyl-naphthalenes are not easily accessible. However, we happened to have a suitably substituted *hetera*-naphthalene at hand. In 2,2-difluoro-4-isopropyl-5,7-dimethoxy-8-methyl-1-oxa-3-oxonia-2-borata-naphthalene (**1**) [22] the *peri* positions under consideration (positions 4 and 5) are occupied by isopropyl and methoxy. The additional 7-MeO group is sterically insignificant [23]. The 8-Me group, though formally in a *peri* position, is not significant either, because O(1) is devoid of a *peri* substituent with which the Me group might interact. B(2), though a tetrahedral centre, does not preclude planarity of the “naphthalene” system [24]. The latter would experience some deformation because of the angle O(1)-B(2)-O(3) < 120°, albeit only in a region far



from the C(4)/C(5) *peri* space. The F atoms at B(2) would reside above and below the C₇BO₂ plane, hence again in sterically unimportant environments.

On the other hand, **1** is an interesting compound for two additional reasons, first in view of the alleged “dative” bonds N→Si/P believed to be capable of assuming any length between the sum of the covalent radii, $\Sigma r_{\text{cov}}(\text{N}, \text{Si/P})$, and $\Sigma r_{\text{vdW}}(\text{N}, \text{Si/P})$ *ad libitum*. The term *dative bond* and its symbol, N→Si/P in silicon and phosphorus chemistry, were adopted from the chemistry of tetracoordinate boron where they had been in widespread use. For N→B bonds, too, the idea has been promulgated that their lengths can cover the entire range from $\Sigma r_{\text{cov}}(\text{B}, \text{N})$ to $\Sigma r_{\text{vdW}}(\text{B}, \text{N})$, *viz.* 157 - 291 pm [25]. In **1**, one

of the bonds emanating from B(2), B(2)-O(3) as a first choice [26], could be envisaged as a dative bond (see formula **1A**) so that the structure of **1** is likely to provide information about the properties of such bonds. Second, deprotonation of the methine carbon atom of the Me₂(H)C group would yield the anion **2** which should benefit energetically by a very efficient resonance of the enolate type, **2A** ↔ **2B**; the methine hydrogen atom should therefore be exceptionally acidic and thus qualify for C-H...X hydrogen bonds. The geometrically enforced proximity of the 5-MeO group might add to the understanding of C-H...O hydrogen bonds which presently raise considerable interest [27].

Results and Discussion

For the discussion of the structure of **1** (Fig. 1), comparison with the difluoroboron chelate of a 3-aryl-4-hydroxy-pent-3-en-2-one (**3**) [24] and the diphenylboron chelate of salicylaldehyde (**4**) [28] (*i. e.* the 4,5,7,8-unsubstituted congener of **1**, except for phenyl groups rather than fluorine atoms at B(2)) is worthwhile. In the carbocyclic ring of **1** and **4**, the C-C bonds emanating from C(10) are significantly longer (**1**: d(C-C) = 143.2 and 143.6 pm, **4**: 142.1 and 140.3 pm) than the remaining C-C bonds (**1**: 137.4 - 139.7 pm, **4**: 136.4 - 139.3 pm). As **1** and **4** are oxonium derivatives of aromatic carbonyl compounds, it is noteworthy that no such conspicuous differences occur, *e. g.*, in benzil (d(C(1)-C(2/6)) = 138.7 and 140.7 pm [29], compared with the remaining C-C bond lengths ranging from 136.3 to 139.6 pm). In **1**, the two elongated bonds include the smallest C-C-C angle (116.7°; **4**: 119.5°; in benzil 119.2°), but the angle C(7)-C(8)-C(9), 116.9° (**4**: 118.7°), is only insignificantly larger; in the latter case, the deviation from 120°, slightly exceeding that in **4**, might be a consequence of the steric hindrance in the C(4)/C(5) *peri* region (*vide infra*). The angle C(5)-C(6)-C(7) at the unsubstituted carbon atom, 119.4° (**4**: 118.8°), is closest to 120° whereas the remaining angles are enlarged by 1.0 to 3.0° (**4**: *ca.* 0 to 2.7°). The third bond emanating from C(10), C(4)-C(10), 141.4 pm (**4**: 140.9 pm), comes reasonably close to C(5)-C(10) and C(9)-C(10), but is significantly shorter than the corresponding bond in benzil (d(OC-C(1)) = 144.9 pm).

The heterocyclic ring deviates more strongly from a regular hexagon. This is caused by greater

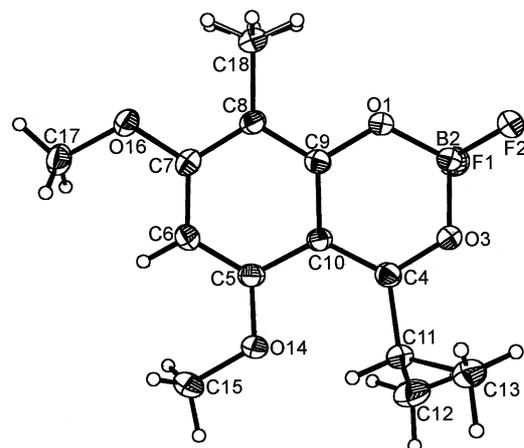


Fig. 1. Crystal structure of **1** with numbering of atoms (50% probability ellipsoids; the disorder of the hydrogen atoms at C(18) is indicated by filled and open bonds).

differences of bond lengths as well as by the angles around B(2) which largely maintains its “natural” tetrahedral environment with bond angles ranging from 107.3°/107.7° (F-B(2)-O(3)) to 111.6° (F-B(2)-F) (**3**: from 108.2° (F-B(2)-O(1/3)) to 111.1° (F-B(2)-F); **4**: from 107.6°/107.9° (Ph-B(2)-O(3)) to 113.3° (Ph-B(2)-Ph)), one of the F-B(2)-O(1) angles (109.5°) and the endocyclic angle O(1)-B(2)-O(3) (109.2°) being virtually ideal tetrahedral angles (**3**: F-B(2)-O(1/3) 109.1°/109.9°, O(1)-B(2)-O(3) 110.0°; **4**: Ph-B(2)-O(1) 109.1°, O(1)-B(2)-O(3) only 107.5°). It is noteworthy that in the adduct of 2-methyl-acroleine and boron trifluoride, H₂C=C(Me)-C(H)=O⁺-B⁻F₃, the deviations from the tetrahedral angle are much larger (O-B-F 103.9, 104.6, 106.8°, F-B-F 111.1, 114.3, 115.1° [30]). The shortest bond, the carbonyl-type bond O(3)-C(4) (d = 128.8 pm), is considerably longer than the carbonyl bond in benzil (d(C=O) = 121.5 pm) and even almost 3 pm longer than the corresponding bond in **4** (126.1 pm); it is only 5 pm (**4**: 7 pm) shorter than the “single” bond O(1)-C(9) (**1**: d = 133.8 pm, **4**: 133.2 pm) which, in its turn, compares reasonably well with the two exocyclic O-C_{arom.} bonds in **1** (d(C(5)-O(14)_{MeO}) = 135.0 pm; d(C(7)-O(16)_{MeO}) = 134.8 pm). Within the frame of classical resonance theory, the elongation of O(3)-C(4) can be ascribed to a particularly efficient electronic interaction between *two* MeO groups and a carbonyl group whose electron accepting power is enhanced by the oxonium character of its oxygen atom (*cf.* formulae **1B** and **1C**). In **4**, the O(3)-C(4)

bond has the same length as the corresponding bond in the 2-methyl-acroleine/BF₃ adduct (126.1 vs. 126.4 pm) [30]. The forshortening of the C(4)-C(10) bond relative to the C_{Ph}-CO bond in benzil can then be ascribed to an increased resonance between the aromatic C₆ ring and the “carbonyl” oxygen atom, though neither the comparison of the C(4)-C(10) bond lengths in **1** (141.4 pm) and **4** (140.9 pm) nor the C(5)-O(14)_{MeO} and C(7)-O(16)_{MeO} bond lengths, compared with the corresponding data of 1,8-di(methoxy)naphthalene (135.9 pm [21b, 31]), indicate an additional influence of the two MeO groups in **1**. Not surprisingly, the O(1/3)-C(6/4) bonds (129.6, 129.6 pm) and the C(5)-C(4/6) bonds (138.2, 138.2 pm) in **3** have been found to be identical [24], the O(1/3)-C(6/4) bonds being of equal length as the mean length of O(1)-C(9) and O(3)-C(4) in **4**.

In view of the alleged capability of N→B [25] and N→Si/P “dative” bonds to assume any lengths between Σr_{cov} , and Σr_{vdW} it is noteworthy that the two B(2)-O bonds in **1** and **4** exhibit normal lengths of covalent bonds and that there is a comparatively small difference between O(1)-B(2) and B(2)-O(3), the bond which qualifies best for being called a *dative bond* (**1**: d = 145.0 pm / 150.9 pm, **4**: 149.6 pm / 156.9 pm). In fact, the difference of the lengths of the two B-O bonds (**1**: 5.9 pm, **4**: 7.3 pm) is less than that of the lengths of the O⁺-B⁻ bonds in **1** and the 2-methyl-acroleine / BF₃ adduct (158.7 pm [30]). In **1**, the difference of 6 pm is unimpressive in view of the lengths of the B-O bonds in two fused 2,2-difluoro-1,3-dioxo-4,6-diaza-2-borata-5-cobalta-cyclohexanes, d(B-O) = 147.0 - 149.8 pm [32], *i. e.* intermediate lengths. Similarly, d(B(2)-F) = 136.9, 137.9 pm falls into the range of the values in the cobalta-cyclohexanes (135.7 - 139.4 pm). Very similar B-F distances have been reported for **3** (135.2, 136.7 pm) [24] and for the 2-methyl-acroleine/BF₃ adduct (132.4, 136.6, 136.9 pm) [30].

In the C(4)/C(5) *peri* region of **1**, one of the bay angles, O(14)_{MeO}-C(5)-C(10), 116.3°, is significantly smaller than 120°, but the angles C(4)-C(10)-C(5), 125.0°, and C(11)_{methine}-C(4)-C(10), 126.1°, are strongly enlarged so that a splay angle of +7.4° results. For substituents with heteroatoms bearing lone pairs such as MeO, angles < 120° are a widespread phenomenon. *E. g.*, in 1,8-di(methoxy)naphthalene (splay angle *ca.* 0° [18]), the angles MeO-C(1/8)-C(9) are 117.0° [21b, 31]. In 8-methoxy-

α -naphthoic acid N,N-dialkylamides (splay angles +2.4 - +2.7° [18]), the angles MeO-C(8)-C(9) are only 114.4 - 114.8° [33], though the R₂N-CO group lacks any significant electron acceptor properties and does therefore not qualify for a donor-acceptor interaction between the *peri* substituents. In **1**, this part of the molecule thus exhibits the criteria of steric hindrance; the latter is corroborated by the interatomic distances d(O(14)_{MeO}···C(11)_{methine}) = 278.2 pm and d(C(4)···C(5)) = 252.4 pm, both well beyond PD and d(O(14)_{MeO}···C(11)_{methine}) 4.3 pm longer than the mean value of d(O···O) = 254.5 pm in 1,8-(MeO)₂C₁₀H₆ [21b, 31] and d(H₃C···CH₃) = 293.2 pm in 1,8-Me₂C₁₀H₆ [34]. Correspondingly, the splay angle in **1** is virtually identical with the mean value, +7.5°, of the splay angles of 1,8-(MeO)₂C₁₀H₆ and 1,8-Me₂C₁₀H₆. Due to the lack of a substituent at O(1), the opposite *peri* region should be capable of relieving the C(4)/C(5) *peri* strain by contraction in spite of the Me group at C(8) [35]. Except for 1,4,5,8-tetrasubstituted naphthalenes which by necessity resort to out-of-plane distortion for relief from *peri* strain [35c, 36], *peri*-substituted naphthalenes reflect such contraction by an interatomic distance d(C(4)···C(5)) < PD [21b, 35]. In **1**, though d(O(1)···C(8)) = 233.3 pm is indeed shorter than PD, this criterion is not applicable, because the “forshortening” is mainly caused by the bonds O(1)-C(9) and C(8)-C(9) being considerably shorter than the C(1/8)-C(9) bonds in naphthalene, d = 142.5 pm [37]. Because of the divalency of O(1), only two bay angles exist, so that a splay angle is not available either. However, the angles O(1)-C(9)-C(8), 117.7°, and C(18)_{Me}-C(8)-C(9), 121.2°, add to less than 240°, indicating contraction in response to the steric hindrance in the C(4)/C(5) *peri* region. The angles C(18)_{Me}-C(8)-C(7), 121.9°, and C(18)_{Me}-C(8)-C(9), 121.2°, are virtually identical and thus testify the absence of steric factors in the O(1)/C(8) *peri* region; their slight enlargement compensates the diminution of the angle C(7)-C(8)-C(9) which presumably is another consequence of the angle enlargements in the C(4)/C(5) *peri* region (*vide supra*; sum of the three angles around C(8) 359.6°).

Like **3** [24] the entire molecule **1**, ring atoms as well as substituents, is remarkably close to planarity. *E. g.*, the torsional angles C(18)_{Me}-C(8)-C(9)-O(1), 2.7°, and C(18)_{Me}-C(8)-C(7)-C(6), 176.4°, hardly deviate from the ideal angles, 0 and 180°. Even in the C(4)/C(5) *peri* region, the

displacement of C(11)_{methine} and O(14)_{MeO} from the “naphthalene” plane due to steric interactions is very moderate (torsional angles C(11)_{methine}-C(4)-C(10)-C(5) -9.5° , O(14)_{MeO}-C(5)-C(10)-C(4) -12.2° , O(14)_{MeO}-C(5)-C(6)-C(7) -178.8°). The Me group of the 5-MeO substituent (C(15)) resides in almost perfect *anti* position with respect to the C(4)···C(5) connecting line, thus minimizing interference with the isopropyl group (torsional angles C(15)_{Me}-O(14)-C(5)-C(10) 178.1° , C(15)_{Me}-O(14)-C(5)-C(6) -3.3°). Of the ring atoms, only B(2) and, to a lesser degree, C(4) deviate somewhat from the common plane. Of the two B-O bonds, mainly B-O(1) is affected: The torsional angles between B-O(1) and the bonds C(9)-C(10) and C(9)-C(8) are $+20.7^\circ$ and -162.9° , respectively. The B(2)-O(3) bond, favourite candidate for a “dative bond” and therefore more suspect of nonconformist behaviour, complies much better with the natural geometry of naphthalene (torsional angles B(2)-O(3)-C(4)-C(10) and B(2)-O(3)-C(4)-C(11)_{methine} -7.0° and $+174.9^\circ$, respectively). In fact, the B(2)-O(3) bond is closer to “ideal” behaviour than the C(4)-C(10) bond which deviates from coplanarity with the bonds C(5)-C(6) and C(8)-C(9) by 10.8° and 11.3° , respectively. As a matter of course, the Me groups of Me₂(H)C and one of the F atoms reside outside the plane, but the deviation of B(2) from it even permits the second F atom to assume a position virtually in it (see Fig. 1).

On the other hand, the hydrogen atom of Me₂(H)C does not lie in the plane though well in the *sp* sector. An eclipsic arrangement with respect to the neighbouring bonds permitting the Me groups to reside quasi-symmetrically above and below the molecular plane can be envisaged to be energetically unfavourable. The interplay of forces exerted by the steric demands of the Me groups and by repulsive interactions of the hydrogen atom with neighbouring atoms would then cause some rotation around the C(4)-C(11)_{methine} bond. The deviation of B(2) from the plane renders its two faces nonequivalent, the space “on the boron side” being the smaller one. The Me group “on the B(2) side” would therefore face stronger resistance to an increase of the torsional angle C(5)···C(4)-C(11)_{methine}-C_{Me} than the opposite Me group. The expected result would be an arrangement having one Me group “on the boron side” and the H atom and the other Me group at the opposite face, the H atom in a *sp* position and

both Me groups in the anticlinal (*ac*) sectors, but the “B(2) side” Me group at a smaller torsional angle C(5)···C(4)-C(11)_{methine}-C_{Me} than the opposite Me group. The experimental structure is in complete agreement with this reasoning. While both Me groups reside in the *ac* sectors with respect to the C(4)···C(5) connecting line, the Me group “on the B(2) side” is close to an orthogonal position, the other one not far from the dividing line between the *ac* and the *ap* sectors.

In summary, the structure of **1** can be fully rationalized as the consequence of natural bond lengths and angles plus steric congestion in the C(4)/C(5) *peri* region. The conformation of the isopropyl group exhibits the same features as that of the Me₂N group in DAN-Si/P compounds, *e. g.* in DAN-phosphonium salts [1]. A common cause is then suggested, the bulk of the Me groups being the decisive factor in either case. The *syn* orientation of the N-lone pair in DAN-Si/P compounds would, then, be conditioned by them. Methodically, the existence of this rationalization precludes any conclusion in favour of a N→Si/P interaction.

The O(1)B(2)F₂O(3) unit can be regarded as a BF₄⁻ ion in which two fluorine atoms have been replaced by oxygen atoms, leading to a slightly distorted tetrahedron with four similar boron-heteroatom bonds. It is only in formulae such as **1A** that one of these bonds assumes a special character of a “dative bond”. In fact, no experimental facts suggest that a fundamental difference between this bond and the B(2)-F/B(2)-O(1) bonds exists. In **3** as well as in the aforementioned cobalta-cyclohexanes [32], the symmetrical structures render any assignment impossible which bond is the “dative” one, and yet, in the latter the bond angles around boron deviate slightly more from the tetrahedral angle than in **1** (105.0° (F-B-F) - 117.2° (O-B-O) *vs.* 107.3° (F-B(2)-O(3)) - 111.6° (F-B(2)-F)). The B(2)-O(3) bond is only 4% longer than the O(1)-B(2) bond; its length does not lend support to the concept that “dative” bonds have special properties concerning stretchability [38], in particular to interatomic distances much beyond normal covalent bond lengths. The repercussions for “dative” N→Si/P interactions are obvious.

For the problem of C-H···O hydrogen bonds, the hetero-naphthalene system of **1** is interesting, because PD, much too *long* for any *covalent bond* to be formed between atoms of second and third period

elements without recourse to distortion of the naphthalene system, is much too *short* to accommodate a C-H...O hydrogen bond. The interatomic distances $d(X\cdots Y)$ between the non-hydrogen atoms X and Y engaged in a hydrogen bond X-H...Y are able to vary much more than the lengths of covalent bonds, but must surpass certain minimum distances. *E. g.*, for the very strong hydrogen bond in $H_3N^+-H\cdots NH_3$ $d(N\cdots N) = 285$ pm has been obtained by molecular orbital calculations [39]. In protonated amines, $d(N\cdots N)$ can be somewhat shorter if favourable conditions account for the energetic cost of the compression. In the shortest N-H...N hydrogen bonds, $d(N\cdots N)$ is *ca.* 253 pm [40], *i. e.* slightly longer than PD. In protonated 1,8-bis(dimethylamino)naphthalene, even a very short NH...N bond would force the naphthalene skeleton into some distortion. In fact, $d(N\cdots N) = 256 - 261$ pm [41] and the splay angle between the N-C(1,8) *peri* bonds, $+2.7^\circ$ [16], testify that the cation tolerates a significant deformation of the C₁₀ skeleton more easily than the minimum N...N distance [42]. Similarly, in 8-dimethylamino- α -naphthol $d(N\cdots O) = 257$ pm [43] and a splay angle of $+2.0^\circ$ [16] are evidence that the length of a O-H...N hydrogen bond cannot shrink sufficiently to grant the C₁₀ system relief from deformation. In sp^3 -C-H...O hydrogen bonds between O acceptors and chlorohydrocarbons, the minimum (mean) distance $d(C\cdots O)$ is 332 pm [44]. In sp -C-H...O hydrogen bonds, mean $d(C\cdots O)$ is 346 pm, the shortest individual value 310 pm; the mean C...O distance in sp^2 -C-H-O hydrogen bonds is 364 pm [45]. An exceptionally strongly C-H acidic compound, *viz.* malonodinitrile, engaged in an unusually short sp^3 -C-H...O hydrogen bond, $d(C\cdots O) = 307$ pm [46]. In (methyl)tri(phenyl)phosphonium 2,6-di(phenyl)-phenolate interionic C-H...O contacts between 302 and 324 pm (average 313 pm) with C-H...O angles from 158 to 174° (average 166°) have been identified and presented as *the shortest C-H...O hydrogen bonds yet determined by single crystal neutron diffraction* [47]. In **1**, the experimental distance $d(O(14)_{MeO}\cdots C(11)_{methine}) = 278.2$ pm, though achieved at the expense of considerable distortion of the C₁₀ skeleton by means of steric hindrance, still falls short of these C...O distances by at least *ca.* 30 pm: The C...O distance required for a C-H...O hydrogen bond remains out of reach. $d(O(14)_{MeO}\cdots C(11)_{methine})$ is in accord with the angle $C(11)_{methine}-H\cdots O(14)_{MeO}$: In all the quoted ex-

amples, the C-H...O hydrogen bonds, even weak ones, exhibit a pronounced tendency towards linearity, mean angles C-H...O around 140° (165 to 180° in alkynes and alkenes) being most frequent and smaller than *ca.* 130° not being observed [44 - 48]. In **1**, the angle $C(11)_{methine}-H\cdots O(14)_{MeO}$ is only 112.0° . This result is in line with Steiner's *caveat* that not all short C-H...O contacts are hydrogen bonds [49]. It is a case of *forced intramolecular contacts* [50] and a complement to the fact that "short" (*e. g.* sub-van-der-Waals) interatomic distances considerably *longer* than covalent bond lengths, if conditioned by geometry as in the *mono-, bi-, tricapped tetrahedra* of DAN-silanes and phosphorus compounds [8, 10, 13, 51, 52], provide no evidence for "bonding".

NMR data may be expected to yield information about the situation in solution. In 1,8-disubstituted naphthalenes rotation around the *peri*-bonds may be facile [35a, 53] or severely hindered [54]. In either case, the geminal Me groups of the Me₂(H)C substituent of **1** are diastereotopic unless there is a rapid flip of the heterocyclic ring. However, even in the 500 MHz ¹H NMR spectrum there is no indication of non-equivalence of the Me groups at 298 as well as at 208 K. The isochrony may be due either to a rapid flip in the O(1)-B(2)-O(3) region or to the considerable distance of the Me₂(H)C group from this region so that the Me groups are accidentally isochronous. The latter is not unlikely, because even the constitutionally different MeO groups give only one sharp singlet at 200 MHz and reveal their non-equivalence only in the 500 MHz spectrum by two singlets separated by only 5.9 Hz at 298 K. The ¹H-coupled ¹³C NMR spectrum exhibits four quadruplets indicating four (not five) different types of Me groups. Since a two-fold accidental isochrony is less probable, a rapid ring flip making the Me groups equivalent may be the preferred explanation. Not surprisingly because of the similar type of bonding, the positions of the ¹⁰B/¹¹B NMR signals resemble those of Et₂O⁺-B⁻F₃ and of Bu₄N⁺BF₄⁻. The ¹⁹F/¹¹B coupling, well resolved in a reference ¹¹B NMR spectrum of Bu₄N⁺BF₄⁻, is not observed in the corresponding spectrum of **1**; the difference reflects fast relaxation processes due to the lower symmetry. Likewise, no ¹⁹F/B coupling is visible in the ¹⁹F NMR spectrum of **1** in which two singlets separated by 12 Hz in the intensity ratio of the natural abundance of ¹⁰B / ¹¹B appear.

Table 1. Crystal data and results of the structure refinement for **1**.

Formula	C ₁₃ H ₁₇ BF ₂ O ₄
MW [g·mol ⁻¹]	286.08
Crystal colour	light yellow
Crystal system	triclinic
Space group	P $\bar{1}$
<i>a</i> [Å]	7.606(1)
<i>b</i> [Å]	9.510(1)
<i>c</i> [Å]	10.708(2)
α [°]	67.16(3)
β [°]	86.50(3)
γ [°]	73.09(3)
<i>V</i> [Å ³]	681.8(2)
Temperature [K]	170
<i>Z</i>	2
<i>D</i> _{calc.} [g·cm ⁻³]	1.394
<i>F</i> (000)	300
2 θ -Range	3 - 52°
<i>h</i> / <i>k</i> / <i>l</i> Ranges	0/9, -11/11, -13/13
μ (Mo-K α) [mm ⁻¹]	0.12
Measured refl.	2887
<i>R</i> _{int.}	0.0137
Independent refl.	2674
Refl. with <i>I</i> > 2 σ (<i>I</i>)	1902
Refined parameters	184
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0317
<i>wR</i> ₂ [all data]	0.0925
GoF	1.038
Min./max. res./e·Å ⁻³	0.25/-0.18

Conclusion

The common conformational behaviour of the isopropyl group of **1** and the Me₂N group in DAN-Si/P compounds makes an electronic interaction N→Si/P in the latter unlikely. The “dative” bond B(2)-O(3) has an unobvious length in the range of normal covalent bond lengths and does not indicate that greatly enhanced lengths of such bonds are possible. The structural properties of DAN-Si/P compounds are, therefore, best attributed solely to the steric situation in their *peri* regions. Our previous conclusions [1, 15 - 18, 38, 55] from other data are thus confirmed.

Experimental Section

2,2-Difluoro-4-isopropyl-5,7-dimethoxy-8-methyl-1-oxa-3-oxonia-2-borata-naphthalene (**1**)

The synthesis of **1** has been described previously [22]. ¹H NMR (500.13 MHz, CD₂Cl₂): 298 K: δ = 1.27 (d, ³J(H,H) = 6.7 Hz, 6H, CH(CH₃)₂), 2.01 (s, C(8)-CH₃), *ca.* 1.8 - 2.2 (m, CH (CH₃)₂), 3.98, 3.99 (2 s, 2 x 3H, 2

Table 2. Selected distances (pm) and bond angles (°) for **1**.

O(1)-C(9)	133.8(2)	O(1)-B(2)	145.0(2)
B(2)-F(2)	136.9(2)	B(2)-F(1)	137.9(2)
B(2)-O(3)	150.9(2)	O(3)-C(4)	128.8(2)
C(4)-C(10)	141.4(2)	C(4)-C(11)	150.6(2)
C(5)-O(14)	135.0(2)	C(5)-C(6)	137.4(2)
C(5)-C(10)	143.2(2)	C(6)-C(7)	139.7(2)
C(7)-O(16)	134.8(2)	C(7)-C(8)	139.7(2)
C(8)-C(9)	138.8(2)	C(8)-C(18)	150.2(2)
C(9)-C(10)	143.6(2)	C(11)-C(13)	152.8(2)
C(11)-C(12)	153.7(2)	O(14)-C(15)	143.5(2)
O(16)-C(17)	144.1(2)		
C(9)-O(1)-B(2)	119.6(2)	F(2)-B(2)-F(1)	111.6(2)
F(2)-B(2)-O(1)	109.5(2)	F(1)-B(2)-O(1)	111.4(2)
F(2)-B(2)-O(3)	107.3(2)	F(1)-B(2)-O(3)	107.7(2)
O(1)-B(2)-O(3)	109.2(2)	C(4)-O(3)-B(2)	121.9(2)
O(3)-C(4)-C(10)	120.0(2)	O(3)-C(4)-C(11)	113.9(2)
C(10)-C(4)-C(11)	126.1(2)	O(14)-C(5)-C(6)	122.7(2)
O(14)-C(5)-C(10)	116.3(2)	C(6)-C(5)-C(10)	121.0(2)
C(5)-C(6)-C(7)	119.4(2)	O(16)-C(7)-C(8)	115.1(2)
O(16)-C(7)-C(6)	121.9(2)	C(8)-C(7)-C(6)	123.0(2)
C(9)-C(8)-C(7)	116.9(2)	C(9)-C(8)-C(18)	121.2(2)
C(7)-C(8)-C(18)	121.9(2)	O(1)-C(9)-C(8)	117.7(2)
O(1)-C(9)-C(10)	119.5(2)	C(8)-C(9)-C(10)	122.7(2)
C(4)-C(10)-C(5)	125.0(2)	C(4)-C(10)-C(9)	118.0(2)
C(5)-C(10)-C(9)	116.7(2)	C(4)-C(11)-C(13)	111.8(2)
C(4)-C(11)-C(12)	109.7(2)	C(13)-C(11)-C(12)	110.1(2)
C(5)-O(14)-C(15)	118.6(2)	C(7)-O(16)-C(17)	118.6(2)

OCH₃), 6.06 (s, 1H, C(6)-H). 208 K: 1.19 (d, ³J(H,H) = 6.7 Hz, 6H, CH(CH₃)₂), 1.90 (s, C(8)-CH₃), *ca.* 1.7 - 2.1 (m, CH(CH₃)₂), 3.89, 3.92 (2 s, 2 x 3H, 2 OCH₃), 5.93 (s, 1H, C(6)-H). - ¹³C NMR (125.76 MHz, CDCl₃): δ = 0.001 (q), 7.32 (q), 19.40 (q), 36.42 (d, CH(CH₃)₂), 56.19 (q), 87.74 (d, C (6)), 104.42, 107.85, 162.99, 163.54, 170.22 (5 s, C(5, 7, 8, 9, 10)), 203.58 (s, C(4)). - ¹⁹F NMR (188.31 MHz, CDCl₃, ref. δ (CCl₃F) = 0): δ = -147.37 (s, ¹⁰B-isotopomer), -147.43 (s, ¹¹B-isotopomer), $\Delta\delta$ = 11.6 Hz. - ^{10,11}B NMR (128.38 MHz, CDCl₃, ref. δ (Et₂O⁺-B⁻F₃) = 0, 297 K): δ = -4.89 (s, ¹¹B), -4.91 (s, ¹⁰B); for comparison: Bu₄N⁺BF₄⁻) (¹¹B, in CD₃CN): δ = -1.38 (p, ¹J(B, F) = 0.5 Hz).

Crystal structure determination

Intensity data were collected using a CAD-4 four-circle diffractometer. The structure was solved with direct methods using SHELXS-97. Structure refinement was done against *F*² using SHELXL-97. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameter using the riding model. The hydrogen atoms attached to C(18) are disordered in two orientations and were refined using a split model. The technical details of

C(9)-O(1)-B(2)-F(2)	-155.4(2)	C(9)-O(1)-B(2)-F(1)	80.6(2)
C(9)-O(1)-B(2)-O(3)	-38.3(2)	F(2)-B(2)-O(3)-C(4)	150.6(2)
F(1)-B(2)-O(3)-C(4)	-89.2(2)	O(1)-B(2)-O(3)-C(4)	32.0(2)
B(2)-O(3)-C(4)-C(10)	-7.0(2)	B(2)-O(3)-C(4)-C(11)	174.9(2)
O(14)-C(5)-C(6)-C(7)	-178.8(2)	C(10)-C(5)-C(6)-C(7)	-0.3(2)
C(5)-C(6)-C(7)-O(16)	-177.0(2)	C(5)-C(6)-C(7)-C(8)	4.1(2)
O(16)-C(7)-C(8)-C(9)	177.9(2)	C(6)-C(7)-C(8)-C(9)	-3.1(2)
O(16)-C(7)-C(8)-C(18)	-2.6(2)	C(6)-C(7)-C(8)-C(18)	176.4(2)
B(2)-O(1)-C(9)-C(8)	-162.9(2)	B(2)-O(1)-C(9)-C(10)	20.7(2)
C(7)-C(8)-C(9)-O(1)	-177.8(2)	C(18)-C(8)-C(9)-O(1)	2.7(2)
C(7)-C(8)-C(9)-C(10)	-1.6(2)	C(18)-C(8)-C(9)-C(10)	178.9(2)
O(3)-C(4)-C(10)-C(5)	172.7(2)	C(11)-C(4)-C(10)-C(5)	-9.5(2)
O(3)-C(4)-C(10)-C(9)	-14.2(2)	C(11)-C(4)-C(10)-C(9)	163.6(2)
O(14)-C(5)-C(10)-C(4)	-12.2(2)	C(6)-C(5)-C(10)-C(4)	169.2(2)
O(14)-C(5)-C(10)-C(9)	174.7(2)	C(6)-C(5)-C(10)-C(9)	-3.9(2)
O(1)-C(9)-C(10)-C(4)	7.5(2)	C(8)-C(9)-C(10)-C(4)	-168.7(2)
O(1)-C(9)-C(10)-C(5)	-178.9(2)	C(8)-C(9)-C(10)-C(5)	5.0(2)
O(3)-C(4)-C(11)-C(13)	34.5(2)	C(10)-C(4)-C(11)-C(13)	-143.5(2)
O(3)-C(4)-C(11)-C(12)	-87.9(2)	C(10)-C(4)-C(11)-C(12)	94.1(2)
C(6)-C(5)-O(14)-C(15)	-3.3(2)	C(10)-C(5)-O(14)-C(15)	178.1(2)
C(8)-C(7)-O(16)-C(17)	177.6(2)	C(6)-C(7)-O(16)-C(17)	-1.3(2)

Table 3. Selected torsional angles (°) for **1**.

the data acquisition and some selected refinement results are summarized in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

Crystallographic data (including atomic coordinates and equivalent isotropic displacement parameters, excluding structure factors) for the structures reported in

this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 178151. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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